ROYAL COLLEGE
OF DENTAL SURGEONS
ONTARIO
Ex Libris The
HARRY R. ABBOTT
MEMORIAL
LIBRARY

R. A. Alloway. D.D.

Montreal

1867

Digitized by the Internet Archive
in 2011 with funding from
University of Toronto

http://www.archive.org/details/chemistrymetall00pigg

DENTAL CHEMISTRY.

CHEMISTRY

AND

METALLURGY

AS APPLIED TO THE

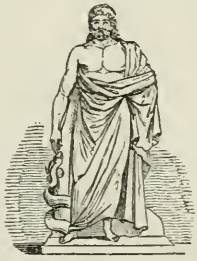
STUDY AND PRACTICE OF DENTAL SURGERY.

BY

A. SNOWDEN PIGGOT, M. D.,

LATE PROFESSOR OF ANATOMY AND PHYSIOLOGY IN THE WASHINGTON UNIVERSITY OF BALTIMORE.

WITH NUMEROUS ILLUSTRATIONS.



PHILADELPHIA:
LINDSAY AND BLAKISTON.
1854.

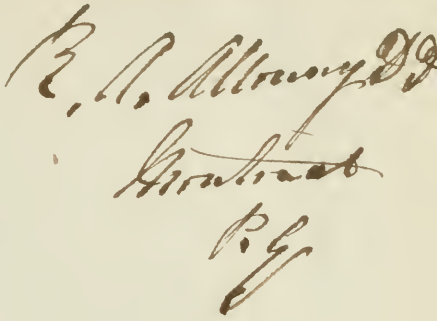
Entered according to the Act of Congress, in the year 1853, by

LINDSAY AND BLAKISTON,

in the Office of the Clerk of the District Court of the United States in and for the Eastern District of Pennsylvania.

PHILADELPHIA:

T. K. AND P. G. COLLINS, PRINTERS.



TO

CHAPIN A. HARRIS, M. D., D. D. S.,

PROFESSOR OF THE PRINCIPLES AND PRACTICE OF DENTAL SURGERY IN THE BALTIMORE COLLEGE,

AS A TOKEN OF RESPECT

FOR HIS

PROFESSIONAL EMINENCE, AND ESTEEM FOR HIS PRIVATE WORTH,

THIS WORK

IS RESPECTFULLY DEDICATED

BY HIS

FRIEND AND OBEDIENT SERVANT,

THE AUTHOR.

PREFACE.

THE following pages were written at the suggestion of several eminent dentists, in whose judgment on all subjects pertaining to dentistry, and especially dental education, the author has the fullest confidence. It was their opinion that a work which should furnish a full account of the chemical principles involved in the various organic changes originating in the mouth, and of the behavior of the metals and other materials used in the workroom, was very much needed by their profession. Whether the present work supplies this demand is for the public to determine.

It is manifest that such a book may be constructed upon one of two plans without losing sight of the original design. It may be adapted either to the wants of the student, who desires to get an enlarged view of the profession upon which he is entering, or it may be confined to those of the practical workman, who demands merely a guide to those manipulations which constitute the round of his daily duty.

In the latter case, all that would be required is a brief statement of those chemical facts which bear directly upon the manipulations alluded to. In the former, a much more extensive field is opened to an author. He cannot, indeed, neglect those practical points, an acquaintance with which is so necessary to the mechanical dentist, but he must not confine himself to them. He must show the connection of this special study with the general science, and point out to the student how it touches the domain of physiological chemistry on the one hand, while, on the other,

it demands an acquaintance with the truths of inorganic chemistry.

It has been the author's aim, in the following pages, to adapt his work to both classes of readers. He has endeavored to make it both a manual for the practical man, and a text-book for the student. He has, therefore, introduced a brief account of the general principles of animal chemistry, which must necessarily form the basis of a successful investigation of any of its specialties. Considering it impossible to get a correct idea of the importance of the mouth and of the processes which take place in it without some knowledge of that great function in which it takes a part, the author has introduced a chemical history of digestion. In his opinion, this forms a necessary preparation for the study of the fluids of the mouth, of which he has given the fullest description in his power.

In regard to the practical details of his work, the author hopes he has been sufficiently precise. So much depends upon the selection and management of fuel, and so many failures result from ignorance of this, and of the best modes of generating and controlling high heats, that a special chapter upon this subject was deemed necessary. In the chapter on the different metals, it is hoped that no important practical suggestion has been omitted. The author would call the special attention of practical mechanical dentists to the chapters on gold, silver, and copper, and particularly to the tables of coins of the two first-named metals, a careful examination of which will enable the maker of plate-work to avoid those crystalline, unmalleable alloys that prove so troublesome, and to be certain of the exact composition of his plate, a point the importance of which it is not necessary to dwell upon. The account of the behavior of the metals is rather fuller than it would have been had a mere manual for the practical man been designed; but as a text-book was also aimed at, it was thought proper to give as complete a history of the metals as the plan of the work would admit of.

The subject of porcelain has received much attention. A full account of the materials used in the manufacture of that beautiful ware has been introduced, for the benefit of those who may wish directly to collect them, and numerous formulæ have been

given for the manufacture of teeth. Those of Dr. A. A. Blandy can be implicitly relied upon, as they have been for some time and are still used by him, with uniformly good practical results.

It has not been thought necessary to encumber the margins of the book with citations. But few references are given, and these, usually when quotations have been made. The author has consulted all the authorities which were accessible to him. He desires especially to acknowledge his obligations to the recent admirable work of Lehmann, the papers of his translator, Dr. Day, in *Ranking's Half-Yearly Abstract* and the *British and Foreign Medico-Chirurgical Review*, Dr. Samuel Wright's articles on Saliva, in the *London Lancet*, and Donaldson's and Porcher's papers on Bernard's recent discoveries, in the *American Journal of the Medical Sciences*, and the *Charleston Medical Journal and Review*. The treatises of Overman and Phillips on Metallurgy, the Dictionary of Ure, the Cyclopædia of Chemistry, by Booth, the works of Liebig, and the various chemical journals have also been freely used.

To Dr. C. A. Harris the author is indebted for many valuable hints, and much important information as to the kind of chemical knowledge the dentist needs. To Dr. A. A. Blandy, Professor of Operative Dentistry in the Baltimore College, he would also express his acknowledgments, for the practical recipes he has furnished him with, and for his kindness in allowing him to witness the various manipulations in his operating rooms.

CONTENTS.

PAGE

Dedication v
Preface vii

BOOK I.

CHAPTER I.—Ultimate Chemical Elements of the Human Body 17–22
Metalloids 19
Metals 20

CHAPTER II.—Proximate Elements of the Body . . . 22–28
Mode of Combination in Organic Substances . . . 22
Compound Radicals 24
Putrefaction 26

CHAPTER III.—The Albuminous Group 28–50
Protein Compounds 29
Albumen 33
Fibrin 37
Globulin 42
Casein 43
Gluten 44
Legumin 48
Teroxide of Protein 49

CHAPTER IV.—The Gelatinous Group 50
Glutin 50
Chondrin 52

CHAPTER V.—Nitrogenous Basic Bodies 53
Creatine 54
Creatinine 55
Tyrosine 56
Leucine 56
Sarcosine 57
Glycine 58

PAGE

Urea 59
Xanthine 63
Guanine 64
Allantoine 64
Cystine 65
Taurine 66

CHAPTER VI.—Nitrogenous Acids 67
Carbazotic Acid 67
Hippuric Acid 67
Uric Acid 68
Inosic Acid 71
Glycocholic Acid 71
Taurocholic Acid 72

CHAPTER VII.—Non-Nitrogenous Acids 73
Butyric Acid Group 73
Oxalic Acid 74
Formic Acid 76
Acetic Acid 76
Metacetonic Acid 77
Butyric Acid 77
Valerianic Acid 78
Caproic Acid 78
Œnanthylic Acid 79
Caprylic Acid 79
Succinic Acid Group 79
Succinic Acid 80
Sebacic Acid 80
Benzoic Acid Group 80
Benzoic Acid 80
Lactic Acid Group 81
Lactic Acid 81
Solid Fatty Acids 83
Margaric Acid 83
Stearic Acid 84
Oily Fatty Acids 84
Oleic Acid 84
Resinous Acids 85
Lithofellic Acid 85
Cholic Acid 85

CHAPTER VIII.—Non-Nitrogenous Bases and Salts—Haloids . 87
Oxide of Lipyl 89
Glycerine 90
Salts of Oxide of Lipyl or Fats 90

PAGE

Lipoids 95
Cholesterin 95
Serolin 96

CHAPTER IX.—Non-Nitrogenous Neutral Bodies . . 96
Glucose 96
Milk-Sugar 99

CHAPTER X.—Pigments 100
Hæmatin 100
Melanin 102
Bile Pigment 102
Urine Pigment 103

BOOK II.

DIGESTION.

CHAPTER I.—Physiological Relations of Digestion . . 103

CHAPTER II.—Food 111

CHAPTER III.—Gastric Digestion 119

CHAPTER IV.—Intestinal Digestion 132
Bile 132
Pancreatic Juice 142
Intestinal Juice 145
Contents of Intestinal Canal and Excrements . . 146

BOOK III.

THE CHEMISTRY OF THE MOUTH.

CHAPTER I.—The Teeth 153

CHAPTER II.—Saliva 157

CHAPTER III.—On the Morbid Changes of Saliva . . 194
Deficient Saliva 194
Redundant Saliva 196
Ptyalism 199
Fatty Saliva 204
Sweet Saliva 206
Albuminous Saliva 207
Bilious Saliva 208
Bloody Saliva 210
Acid Saliva 211

PAGE

Alkaline Saliva 214
Calcareous Saliva 215
Saline Saliva 215
Puriform Saliva 216
Fetid Saliva 216
Acrid Saliva 217
Urinary Saliva 218
Gelatinous Saliva 219
Milky Saliva 220
Changes of the Saliva in Disease 220

CHAPTER IV.—Mucus 222

CHAPTER V.—Salivary Calculi 231

BOOK IV.

CHEMISTRY AND METALLURGY OF THE METALS AND EARTHS USED BY THE DENTIST.

PART I.

THE METALS.

CHAPTER I.—The Different Modes of Applying Heat, Furnaces, and Auxiliary Apparatus . . 235
The Blowpipe 237
Lamps 240
Furnaces 248
Crucibles 254
Cupels 259
Lutes 260
Fuel 261
Measurement of the Heat of Furnaces . . . 275

CHAPTER II.—Gold 278
Metallurgic Treatment of Gold Ores 280
Metallurgy of the Alloys of Gold 284
Goldbeating 300
Alloys and Non-Saline Compounds 303
Alloys of Gold 312
Table of Coinage of Different Nations . . . 316
Salts of Gold 322

CHAPTER III.—Silver 325
Metallurgic Treatment of Silver Ores 326
Amalgamation 326
Smelting 328

PAGE

Metallurgic Treatment of the Alloys of Silver . . . 329
Scorification 329
Cupellation 330
Liquation 335
Crystallization 335
Humid Process 336
Silver, Non-Saline Compounds, and Alloys . . . 341
Alloys of Silver 345
Table of Silver Coins 347
Salts of Silver—Haloid Salts 356
Salts of Silver—Oxysalts 358

CHAPTER IV.—Copper 363
Metallurgic Treatment of Copper Ores . . . 365
Metallurgic Treatment of the Alloys of Copper . . 369
Copper and its Non-Saline Compounds . . . 371
Alloys of Copper 376
Haloid Salts 379
Oxysalts—Salts of the Suboxide 382
Oxysalts—Salts of Black Oxide 383

CHAPTER V.—Zinc 387
Metallurgic Treatment of Zinc Ores 387
Zinc and Non-Saline Compounds 388
Alloys 391
Haloid Salts 391
Oxysalts 392

CHAPTER VI.—Tin 394
Tin and its Non-Saline Compounds 396
Alloys of Tin 400
Haloid Salts 401
Oxysalts 402

CHAPTER VII.—Lead 403
Metallurgy of Lead 403
Lead and its Non-Saline Compounds 405
Alloys of Lead 407
Haloid Salts 408
Oxysalts 409

CHAPTER VIII.—Bismuth 412
Bismuth and its Non-Saline Compounds . . . 412
Alloys of Bismuth 414
Salts 415

PAGE

CHAPTER IX.—Platinum 416
Preparation of Platinum 418
Metallurgy of the Alloys of Platinum . . . 422
Platinum and its Non-Saline Compounds . . . 424
Alloys 428
Haloid Salts 429
Oxysalts 437

CHAPTER X.—Mercury 438
Metallurgic Treatment of Mercurial Ores . . . 439
Mercury and its Non-Saline Compounds . . . 441
Amalgams 444
Haloid Salts 444
Oxysalts 446
Effects of Mercury on the System 446

PART II.

THE MATERIALS USED IN MAKING INCORRUPTIBLE TEETH.

CHAPTER I.—Silicon 450

CHAPTER II.—Aluminum 454

CHAPTER III.—Potassium 457

CHAPTER IV.—Sodium 463

CHAPTER V.—The Materials used for Porcelain Teeth . 466
Clays 466
Feldspar 470
Quartz Sand 473

CHAPTER VI.—Porcelain 473

CHAPTER VII.—Coloring Materials 478
Oxide of Titanium 480
Oxide of Uranium 483
Oxide of Manganese 485
Oxide of Cobalt 486

CHAPTER VIII.—Incorruptible Teeth 487
History 487
Preparation of Materials 488

DENTAL CHEMISTRY.

BOOK I.

GENERAL PRINCIPLES OF ANIMAL CHEMISTRY.

CHAPTER I.

THE ULTIMATE CHEMICAL ELEMENTS OF THE HUMAN BODY.

In treating of any subject connected with animal life, it is exceedingly difficult to decide on our point of departure. All the functions of a living creature are so dependent one upon another, and touch each other in so many points, that it is impossible to isolate one from all the rest, and to treat it as a simple scientific unit. When we are reviewing the entire history of the living body, this difficulty is not so sensibly felt, for we may begin where we please, and we are sure to return to our starting-point if we do but follow the order of succession of the different functions, so true it is that the vital actions move in a circle. In studying a special department of physiological chemistry, however, we are immediately made to feel the necessity of a careful selection of our course, through the abundant materials which lie around us. A segregation of our subject would present an imperfect and limited, and therefore an untrue view of it, while an examination of all its connections with the general life of the body, however desirable to the student who has abundant leisure to devote to it, would, by the extreme and unnecessary expansion to which it would lead, deter many from

a very important and necessary study. In an elementary work like the present, designed especially for students, it is incumbent upon the author to keep these facts in view, and carefully to avoid running into either of these objectionable extremes. We must examine, as minutely as time will permit, the immediate relations of the subject under consideration, and confine ourselves as closely as possible to them.

It is proposed in the following pages to consider the physiological chemistry of the natural organs of mastication, and to examine the chemical principles upon which the success or failure of the artificial substances used by the dentist to remedy defects in these organs will depend. This, of course, includes the study of the chemical composition of the teeth, as well as of the soft parts which surround them, and the secretions which flow over them. When we consider, however, that this apparatus, beautiful and perfect as it is, is but subsidiary to another of the utmost importance to the well-being of the system, we see the impropriety of limiting our view to the mere mouth. Since the health of the mouth is essential to the perfect health of the stomach, and since diseased conditions of the latter cavity react upon the former, it becomes us to understand the function of the one if we would fully comprehend that of the other. Moreover, as these combined functions form but a part of a great organic process, it is necessary to acquire a general notion of the whole before we can accurately determine the importance of the part we are studying. The following pages will, therefore, comprise a general account of the process of assimilation, with a more particular description of the functions of digestion, especially those preliminary parts of it which are performed in the mouth, and the changes, so far as known, which these last undergo in disease. The elementary nature of this work, however, renders it desirable that some general remarks on the constituents of the human body should be prefixed.

The human body, made up, as it is, of a great variety of tissues arranged in an harmonious whole, is nevertheless capable of being resolved into a number of *proximate elements*, which form the basis of all the tissues and secretions of the system. These proximate elements are not, in the chemist's sense of the term,

simple; but are each of them made up of several *chemical* elements. Of the latter substances, *oxygen*, *hydrogen*, *nitrogen*, and *carbon* are found in by far the greatest abundance. These, in varying proportions, form the basis of all the organic tissues and secretions. Their combinations being very complex will form the subject of a future chapter. There are superadded to them many other elements, which shall now be very briefly enumerated.

Sulphur forms a part of almost all the tissues, and composes a very considerable proportion of some of them. In its elemental form it enters into the composition of the very basis of the body, in albumen and fibrin, and into all the tissues compounded of these. It can also be detected in many of the secretions, especially in bile, of one of the component parts of which, taurine, it constitutes twenty-five per cent. In combination with other metalloids and metallic oxides, it exists in less abundance, and is less widely diffused. Thus, we have sulphates in the urine and sweat, and sulphocyanide of potassium has been said to exist in appreciable quantity in the saliva.

Phosphorus is also very generally distributed through the system. Like sulphur, in its elemental form, it constitutes an essential part of the albumen and fibrin. It is found, in very large quantity, in the brain and nervous system as cerebric and oleophosphoric acids, and entering also into the composition of several distinct cerebral fats. It exists also very abundantly as phosphoric acid, in which form it can be extracted from the blood, the bones, the muscles, and the urine. None of the tissues and very few of the secretions are destitute of this element.

Chlorine, too, is very abundant in the animal economy; not, however, in its elemental form. It is found in combination with hydrogen, as hydrochloric acid in the gastric juice, and with sodium and potassium in almost all the fluids and in many of the solids.

Silicon, in the form of silicic acid or silex, is a constituent of the enamel of the teeth, the hair, the saliva, the urine, the blood, &c.

Fluorine was first detected by Berzelius in bones, teeth, and urine. His experiments were much contested, but after a

full discussion and numerous analyses, the question has been finally settled in favor of the views of the great Swedish chemist.

OF THE METALS.

Potassium is found in the blood and all the fluids as a chloride. Sulphate of potassa, as well as of soda, exists in the blood, urine, milk, and sweat. In some of the fluids the sulphates are not naturally present, but are formed during the chemical process of ignition. The blood, lymph, chyle, bile, milk, and urine, as well as the juice of flesh, contain the phosphates both of potassa and soda. In the latter fluid and in milk, the potash salts predominate over those of soda, while the contrary is true of the other liquids named above.

Sodium abounds as a chloride. As a sulphate and phosphate soda is found in company with potassa. As a phosphate it is very generally diffused. The alkaline reaction of many of the fluids is due to the presence of the tribasic phosphate of soda, composed according to the formula HO, 2NaO, PO_5+24HO. According to Enderlin, the phosphate oftenest met with may be stated as 3NaO, PO_5. Phosphate of soda and ammonia, the *microcosmic salt* of the older chemists and of the modern blowpipe manipulators, is formed in large quantity in putrefying animal fluids. Its formula is HO, NH_4O, NaO, PO_5+8HO.

Calcium is found more largely than any other metal in the body. Its chloride is a constituent of the gastric juice and of the saliva, and its fluoride of the tissues and fluids mentioned above under the head of fluorine. As an oxide (lime) combined with acids, it is more abundant than in any other form. Phosphate of lime is a component part of lymph, chyle, blood, milk, urine, feces, &c. Its principal seat, however, is in the bones and teeth. There it exists in the form of bone-earth, as it is commonly termed, consisting of 48.45 per cent. of acid and 51.55 of base. Its empirical formula, consequently, is 8CaO+ $3PO_5$; but it has been thought to consist of two tribasic phosphates, and therefore to be 2CaO, HO, PO_5,+2 (3CaO, PO_5). In the urine, it is a superphosphate. Carbonate of lime occurs in the bones, teeth, &c., and in morbid concretions, as the

calcareous masses which block up the old cavities and bronchial glands of consumptive patients.

Magnesium is also a component of the human frame, and is very generally distributed, though not in such large proportion as the last-named metal. *Carbonate* of magnesia was supposed by Berzelius to be the form in which this earth exists in bone, the phosphate being formed in the process of analysis, magnesia having, as every chemist knows, a much stronger affinity for phosphoric acid than lime or any of the ordinary bases. This salt also forms a part of the alvine dejections and other excretions. The phosphate is, as might be expected, found in the urine, and it is in the form of this salt that magnesia is obtained from the bones. The ammoniaco-magnesian phosphate is tribasic, with twelve atoms of water, ten of which may be expelled without loss of ammonia. Its formula is, therefore, NH_4O, $2MgO$, $PO_5+2HO+10HO$. It is obtained from diseased urine, urinary calculi, and the feces of patients laboring under typhus fever.

Alumina is found in the teeth, and was said by Orfila to exist in the bones. Lehmann denies its presence in the animal economy.

Iron is a constituent of hæmatin, the coloring matter of the blood, of lymph, chyle, muscles, bones, and many other tissues. Its chloride forms a part of the gastric juice. Its phosphate is supposed to exist in the hair, the pigment-cells, and some of the fluids.

Manganese is contained in the hair, a fact which can be easily demonstrated by fusing the ash of hair with carbonate of soda, when the characteristic green tint of manganate of soda will be observed. It has also been detected in bile and in gall-stones, and it has been asserted that this metal has been obtained from healthy blood.

Copper is reckoned by Devergie, Orfila, Heller, and others as a normal constituent of the soft parts of the blood. There is no doubt of its existence in gall-stones, and it has been fully proved to be a component part of bile.

Lead has also been detected in the body, and at one time Orfila affirmed that *arsenic* was an element of healthy human

bone. An amusing example of the earnestness of his faith in this doctrine took place on the trial of the celebrated Madame Laffarge. On that occasion Orfila was cited as a witness for the defendant. The case hinged upon the question whether the arsenic which was detected about the body, coffin, and earth of the grave had been derived from poison introduced into the stomach of M. Laffarge. Orfila contended that it had not, and in reply to some chemical testimony adduced by the prosecution, in a sudden burst of indignation, he exclaimed: "Why, Mr. President, I can take you off your seat, boil you, and obtain sufficient arsenic from you to exhibit to this jury!" He has, however, since abandoned that idea.

CHAPTER II.

THE PROXIMATE ELEMENTS OF THE BODY.

The organic constituents of the human body, whether solids or fluids, are, as already stated, formed from two or more of the metalloids, oxygen, carbon, nitrogen, and hydrogen, with or without the addition of sulphur and phosphorus.

There are certain peculiarities about the union of these elements in vital chemistry which demand notice in an elementary work like the present. One of these peculiarities has been rather broadly stated. It has been said that in inorganic bodies the common combination is binary, while in organic compounds it is ternary or quaternary; that is to say, these elements unite in the one case in twos, in the other in threes or fours. A little consideration, however, will show that this is not absolutely true. Thus, ethyl, which is an organic radical, is binary, being a carbohydrogen, while chromic alum, a purely inorganic compound, is ternary, being made up of sulphuric acid, oxide of chromium, and alumina.

It is true, however, that the mode of combination in the inorganic is much more simple than in the organic world. We may

illustrate this by the commonly quoted case of carbonate of ammonia. To express this by chemical notation, we may arrange the elements as (CO_3NH_4)* without giving any idea of the mode of union, but simply expressing the atomic constitution of the compound. But upon examination, we detect a definite arrangement of these elements. If we boil this substance with a paste made of recently slaked lime, in a vessel communicating with water, we shall find the liquid in the receiver becoming gradually charged with the volatile alkali (NH_4O), ammonia, while a white powder subsides in the retort. If we now direct our attention to this precipitate, we shall find that it effervesces with acids, giving off a gas which colors litmus paper red, and which, by the application of the proper tests, is ascertained to be carbonic acid (CO_2). Now, if we connect again the different pieces of the apparatus, so that the acid gas shall pass through the alkaline solution, we reproduce the identical substance first experimented on. This completes the proof that the compound consists of carbonic acid and ammonia directly combined. The formula, therefore, will be NH_4O, CO_2, and this is a type of the binary method of combination, so common in inorganic nature.

An organic substance submitted to the same operations yields a totally different result. If to a concentrated solution of urea nitric acid be added, a sudden crystallization reduces nearly the whole solution to a mass of fine leaves or scales. Nothing escapes as in the previous example, and we have to examine the liquid and the crystalline product to ascertain what changes have taken place. In the former, we find nothing but the excess of urea or of nitric acid, as the case may be. In the latter, we detect precisely the same substance as before, with the addition of nitric acid. If we add to the nitrate of urea, thus obtained, oxalic acid in solution, we shall find the nitric acid gradually

* In stating this example of inorganic combination, no distinction has been made between the gaseous ammonia, NH_3, and the oxide of ammonium, NH_4O, which forms the basis of ammoniacal salts; because the full account of these complicated reactions would have only obscured the subject, and diverted the mind of the reader from the main point, viz.: the illustration of the method of combination in inorganic nature.

appearing in the solution, and the oxalic acid taking its place in the salt. Now, this process is diametrically opposite to the former. Urea is found to behave precisely as lime or any other metallic oxide would do, constituting what chemists call a salifiable base, that is, a substance capable of being converted into a salt by the addition of an acid or a metalloid halogen. If, however, we subject urea to the action of heat, we decompose it, and by a series of processes, resolve it into its original elements, and no binary combinations take place except those which are manifestly the result of decomposition and recomposition in the changing substance. Manifestly, the elements in this compound, are united in a manner entirely different from that in which they exist in the example cited from the inorganic world. Our notation must also differ. We express the entire compound in a single unbroken formula, $C_2N_2H_4O_2$.

There is another difference between organic and inorganic compounds, which is always taken into consideration when estimating the difference between these two classes of bodies. In inorganic nature, the elements are usually united in a small number of atoms. Thus, water contains only one atom of hydrogen and one of oxygen; carbonic acid, one of carbon and two of oxygen; muriatic acid, one of hydrogen and one of chlorine. Organic compounds, on the contrary, are far more complex in their composition. Creatine, for example, the crystalline element of watery extract of flesh, contains, according to Liebig, eight parts of carbon, three of nitrogen, eleven of hydrogen, and six of oxygen ($C_8N_3H_{11}O_6$), and the formula for protein ($C_{40}H_{30}N_5O_{12}$) is still more complex.

The peculiarity which these compounds possess of acting towards alkalies and acids like the common bases is one of the most remarkable facts in organic chemistry. The theory of their combination is known as the doctrine of compound radicals. It is one of the recent and most striking developments of this doctrine that one substance may be substituted for another, in these remarkable bodies, without materially changing the relations of the compound to other reagents. Hoffman's brilliant discoveries have disclosed the fact that organic compound radicals may be substituted for the hydrogen of ammo-

nia, and yet the new substance retain many of the marked properties of the original compound. Thus, three atoms of ethyl, which is the organic base of ether, may take the place of the three atoms of hydrogen, so that the formula would be $N(C_4H_5)_3$ instead of NH_5. So we may have a tetrethylammonium or $N(C_4H_5)_4$ instead of NH_4; and even more than this, several organic radicals may be present in a new compound, each one intruding itself in the place of one of the atoms of hydrogen, and yet the general features of ammonia and ammonium be still recognizable.

By an examination of these facts, we can easily discover the reasons of the remarkable instability of organic compounds. It is well known that the larger the number of atoms which enter into the constitution of a body, the greater is its proneness to decomposition. Thus, protoxide of chromium, which contains one atom of oxygen, can be deprived of its oxygen only by carbon and the strong heat of a blast furnace; while chromic acid, which contains three atoms of the metalloid, is reduced to a protoxide by the mere presence of alcohol and a free acid at the common temperature of the atmosphere, or when isolated, by simple contact with any organic body. Besides, the organic compounds of the human body usually contain nitrogen, and that not in the form of nitric acid or ammonium, which are its most stable combinations, and, consequently, those to which it tends. This we know is the most unfixed element in nature. Held to other bodies by a weak affinity, gaseous in its form, it is easily disengaged from its combinations. Chloride of nitrogen, the most terribly explosive substance known, is an example of this powerful tendency to almost spontaneous decomposition. The slightest jarring of this oily compound produces a tremendous explosion. This disposition is very much increased in organic bodies by the presence of the elements of water, which furnish precisely those conditions most favorable to change in the relations of this metalloid.

This extreme mobility of atoms is essentially necessary to these substances, because they require countless modifications to meet the ever-varying necessities of the system, and these modifications must be impressed upon them by feeble, delicate, but constant chemical agencies.

The progress of putrefaction very well illustrates this extreme mobility of particles. In order that this process should begin and continue, nothing more is necessary than that atmospheric air, a due degree of heat, and organic matter, itself in a state of change, should be present. It is well known that the act of fermentation has been for a long time the subject of a warm dispute between the disciples of Liebig and the microscopists.

The discovery of the yeast-plant, and the apparently direct influence of the growth of that infusorial vegetable upon the process of fermentation, led to the hypothesis that all these changes depended upon the growth of microscopic beings in the fermenting or putrefying fluids, and that their results were nothing but the secretions and excretions of these minute organisms.

The experiments of Helmholtz, however, seem decisive upon this point. This observer found that, when animal matter was boiled, and subjected to the action of air which had passed through a *redhot* tube, no change took place, though the substances experimented on were subjected to the influence of oxygen for eight weeks in the heat of summer. As soon, however, as these same fluids were exposed to the *open air*, putrefaction took place, and multitudes of infusoria were found in the decomposing liquids. This would seem to favor the microscopic theory, but our inquirer did not stop here. He subjected the same substances to the action of oxygen produced by the decomposition of water by the electric current, and still no change took place. It is, therefore, manifest that putrefaction in the open air must depend upon some constituent of the atmosphere which is destroyed or modified by a red heat. Now, infusorial germs of living creatures and putrescent exhalations from dead organic matter were considered by him to be the only substances to be found in this class. To determine which of these formed the exciting cause of putrefaction, he resorted to another series of experiments. He took the same substances as before, and introduced into them other putrefiable fluids which had not been excluded from the air. This he did through the pores of a bladder which the smallest infusorial germs could not penetrate. Under these circumstances, he found that putrefac-

tion went on with as great rapidity as when the fluids were directly exposed to the action of the atmosphere, with this difference, however, that they remained clear, and contained no infusoria. He therefore concluded that this great chemical change can be effected in a substance, simply by the presence of another undergoing decomposition, the motion already existing among the particles of the latter producing the same molecular change among those of the former, and predisposing it to the absorption and assimilation of oxygen, by means of which the new products of these changes are formed. The discovery of *pyrrhine* and the investigation of its properties give additional probability to the results of Helmholtz. Of Liebig's reply to his theory of *fermentation*, we have nothing to say at present, as it does not concern the question we are discussing.

The tendency of all these decompositions and recompositions is to the production of compounds of greater stability. Thus, we always find carbonic acid, ammonia and its carbonate, resulting from the decomposition of animal bodies; and usually sulphuretted, carburetted, and phosphuretted hydrogen, together with cyanogen and hydrocyanic acid. The presence of these latter substances has, however, been denied by Mr. Walter Lewis, of London, on the strength of certain experiments and analyses made by him in vaults and catacombs. He could detect nothing in the air of the coffins which he examined except nitrogen, ammonia, carbonic acid, common air, and animal matter in suspension. The corrosions of the lead coffins were always found to have been accomplished by carbonic acid, no traces of either sulphuric acid or sulphuretted hydrogen being found in them.

If, now, we proceed to inquire how these elements are put together in the animal economy, we shall, at first sight, be struck with the very marked difference between the tissues themselves and the secretions. Formed, as they are, from the same common mass of blood, we find, nevertheless, that the tissues invariably contain nitrogen, while the secretions are often deficient in this ingredient. This has led to a general division of the substances, composing the body, into two great classes, the *azotized* and *non-azotized* compounds. The former class is again

subdivided into *excreted* and *histogenetic* substances, and these last into the *albuminous* and *gelatinous* groups. The first of these groups is characterized by very decided peculiarities, to which we shall now briefly advert.

CHAPTER III.

THE ALBUMINOUS GROUP.

One of the great steps which animal chemistry has made, is the discovery of the identity of the forms of this group in the two great divisions of the organic world. The freshly expressed juice of vegetables allowed to stand becomes turbid, and a separation of its constituents takes place. A green gelatinous precipitate falls, which, after the removal of the coloring matter, remains as a grayish mass. This spontaneous coagulation, so closely resembling that which occurs in blood, has caused the name *vegetable fibrin* to be applied to the substance under consideration.

The green parts of vegetables being crushed afford a juice which is not clarified by filtration, and not readily by the process above described. The fluid remaining after the coagulation of the fibrin may be subjected to the temperature of 140° or 160°, when it will coagulate in the same manner as serum or white of egg. This, purified by the removal, by ether, of the green fatty matter which is entangled in its meshes, is *vegetable albumen*.

"When peas, beans, or lentils are softened in cold water, then ground with that fluid, and the mass farther diluted and strained through a fine sieve, there passes through a solution of casein, which is always like milk, turbid, partly from suspended fat, partly from the gradual action of the air on the dissolved casein, lactic acid being slowly formed, which causes a gradual separation. This solution has all the characters of skimmed milk; it is coagulated by acids, not by heat, and forms a pellicle when

heated. It also coagulates after long standing, from the formation of lactic acid; and, when the coagulum putrefies, the odor is exactly that of putrid cheese." This is, of course, *vegetable casein*.

"The chemical analysis of these three substances has led to the very interesting result that they contain the same organic elements united in the same proportion by weight; and what is still more remarkable, that they are identical in composition with the chief constituents of blood, animal fibrin, and albumen.

"They all three dissolve in concentrated muriatic acid with the same deep-purple color, and even in their physical characters animal fibrin and albumen are in no respect different from vegetable fibrin and albumen. It is especially to be noticed that, by the phrase identity of composition, we do not here imply mere similarity, but that even in regard to the present relative amount of sulphur, phosphorus, and phosphate of lime, no difference can be observed."*

PROTEIN COMPOUNDS.

These are all called *protein compounds*, after Mulder, who claims to have discovered a substance from which they may all be formed by the addition of varying proportions of sulphur and phosphorus. To this he gave the name protein (from πρωτευω, I take the first rank). This theory of his, at first adopted and afterwards controverted by Liebig, has led to sharp and animated discussions between him and the adherents of the Giessen school. A brief statement of the theory itself and the discoveries upon which it is based, followed by an account of Liebig's objections, will put the whole subject in an intelligible form.

Mulder says that such a process, as is about to be described, will give us protein in a state of purity. Any one of the albuminous group of proximate elements, albumen, fibrin, or casein, is to be washed first with water to separate soluble salts and water extractive, then in alcohol to get rid of substances soluble in that menstruum, and lastly in ether to dissolve the fatty mat-

* Liebig, Animal Chemistry.

ters which are always present. Dilute hydrochloric acid is then added, and the substance is digested in it till the phosphate of lime is all taken up. If now it be dissolved in a solution of caustic potash at 120° F., two new substances make their appearance in the fluid, sulphuret of potassium and phosphate of potash. Acetic acid is now added very carefully to exact saturation, the precipitate thrown on a filter and washed till the rinsings no longer leave a residue upon evaporation on platinum foil.

The substance thus obtained is, when moist, in grayish flocks, which dry to an amber-colored powder. It differs from that which was originally subjected to the operation. It is insoluble in water, alcohol, or ether, tasteless and inodorous. It burns when exposed to the air without leaving any ash. If boiled, with free exposure to atmospheric air, it is oxidated. It is soluble in dilute acids, forming a compound with them which is precipitated by an excess of acid. Acetic acid and the tribasic variety of phosphoric acid, however, form an exception to this rule, and dissolve it in all proportions. It is precipitated by alkalies, metallic salts, ferrocyanide and ferridcyanide of potassium, tannin, and absolute alcohol.

From these properties Mulder was led to believe that he had obtained a new organic radical by the separation of sulphur and phosphorus from the original albuminous substance, and that consequently, this group was formed by the simple addition of one of these metalloids to this fundamental radical. He found its composition to be

Oxygen	23.3
Carbon	55
Hydrogen	7.2
Nitrogen	14.5
	100.

From this, he deduced the formula $C_{40}H_{31}N_5O_{12}$. He has subsequently repeatedly changed it. Another of his formulæ (proceeding upon the basis of the atomic weights, oxygen 100, carbon 76.437, hydrogen 6.24, nitrogen 88.36) is $C_{40}H_{62}N_{10}O_{12}$.

His latest formula is $C_{36}H_{25}N_4O_{10}+2HO$. Liebig's formula, during the time that he recognized Mulder's discovery, was $C_{48}H_{35}N_6O_{14}$. The symbol is Pr.

To this theory of Mulder, it is objected first, that, as it is nearly if not quite impossible to obtain chemically pure albumen, fibrin, or casein, so it must be equally or even more difficult to isolate, with any kind of precision, their base or radical. Not one of these bodies has ever been exhibited in a chemically pure soluble state, so that any deductions as to their ultimate composition must at this time be premature.

Besides, it is urged that Mulder has not succeeded in doing what he attempted to do; that is, in effecting a total separation of sulphur and phosphorus from fibrin or albumen. He has himself discovered that, under certain circumstances, albuminous bodies, though containing sulphur, might fail to give any evidence of it, when interrogated by the ordinary reagents. *Protein* is in this condition. The potash with which it was boiled has rendered it impossible to appreciate its sulphur by the ordinary tests; but more delicate means of research have shown this metalloid to be still present, and Mulder himself has detected it.

In reply to this objection, Mulder declares that the sulphur is found as hyposulphurous acid, resulting from an imperfect decomposition of the albumen, fibrin, or casein which has been employed in the manufacture of protein. He thinks the sulphur in these compounds is first united with amidogen, and then combined with the protein as sulphamide; so that, when treated with potash, two atoms of sulphamide (NH_2S) combine with two atoms of water, forming ammonia, which escapes, and hyposulphurous acid, which combines with the non-sulphurous atomic group to form those compounds that yield no sulphur reaction with silver.

Lehmann uses the following language in regard to this opinion of Mulder:—

"It certainly is true that all these compounds, on being digested with the fixed caustic alkalies, develop ammonia, and that those yielding the sulphur reaction contain more nitrogen than those which do not exhibit it. The assumption of the presence of sulphamide in these substances must, however, still

be regarded as a somewhat hazardous hypothesis; in the first place, because we are as yet wholly unacquainted with this sulphamide, whether in an isolated or combined state; secondly, because a combination of hyposulphurous acid with an organic scarcely basic substance is as unlooked for a phenomenon as that it should not be separated by stronger acids from its combination with the protein; and lastly, because the hyposulphites yield a most evident sulphur reaction when heated with organic substances on silver foil.

"Mulder, in like manner, assumes that the phosphorus contained in albumen exists in the state of *phosphamide*, H_2NP, a purely hypothetical body, and totally different from Gerhard's phosphamide, whose amide nature is, moreover, very doubtful. These are some of the grounds on which we have been led to regard Mulder's view as a mere scientific fiction."

This is the present state of the protein controversy, a discussion which has rallied the most powerful and acute minds on one side or the other, and which has been productive of great collateral benefit to organic chemistry, from the stimulus it has given to research, and the new facts it has elicited. Mulder has himself admitted that some of his early generalizations, as, for example, the proportioning of protein, phosphorus, and sulphur in the different histogenetic substances, were too hasty. Whatever view, however, may be taken of the possibility of isolating protein, chemists are generally agreed in regarding the hypothesis as a valuable one in the classification of the proximate elements of the body; and the term *protein-compounds* is used by the most decided opponents of Mulder's theory.

These compounds possess some remarkable properties in common. Most of them exist in two modifications, a soluble and an insoluble. The soluble modification, when dry, is yellowish and translucent, and devoid of taste or smell. It is soluble in water, but insoluble in alcohol or ether, and when once precipitated by alcohol from its solution in water, it usually loses its solubility in the latter menstruum. The watery solution is precipitated by the metallic salts, the acid of which is commonly found in the precipitate. The majority of them are not precipitated by alkalies or vegetable acids, but by mineral acids,

except the phosphoric and by tannic acid. They are converted into the insoluble form by boiling or by precipitation with the mineral acids.

The *insoluble compounds* when dry are white, tasteless, and inodorous; insoluble in water, alcohol, or ether, but soluble in alkalies, from which they are precipitated by neutralization with acids. Acetic and organic acids generally dissolve them, and both *ferrocyanide* and *ferridcyanide of potassium* precipitate them from these solutions. The concentrated acids do not dissolve them, but form with them compounds insoluble in acidulated water, but soluble in pure water, after first swelling and becoming gelatinous in appearance. Concentrated *nitric acid* turns them yellow; strong hydrochloric acid, with free access of air and moderate warmth, gives them a fine blue color. Millon's test, said to be the most delicate, is made by dissolving one part of mercury in two parts of nitric acid containing four and a half equivalents of water. The substance to be tested, after having been mixed with this fluid, or moistened with it, if it be a tissue, is then heated to between 140° and 212°, when it acquires a deep-red tint not to be dispelled by prolonged boiling or exposure to the air.

ALBUMEN.

Among the histogenetic substances albumen is of the very first importance. It is undoubtedly the origin of the different tissues.

Lehmann and Scherer have shown that albumen varies very much with the source whence it has been derived, owing to certain adventitious admixtures. Thus, the albumen of the blood differs from that of the egg; the albumen of a hen's egg from that of a dove's; and the albumen of one man's blood from that of another's; and that of the blood of the same man even differs at different times. These variations are not only confined to the saturating capacity of these different albumens, but extend to their chemical constitution, more especially their proportion of sulphur. Albumen may be studied in two forms, which we have just shown to be common to all protein compounds, the soluble and insoluble modification.

Soluble albumen, dried in the air, is a pale-yellowish, translucent mass, easy of pulverization. The specific gravity of the albumen of the hen's egg has been ascertained to be 1.3144; or after calculation, rejecting the salts, 1.2617. It becomes positively electric by friction. It is inodorous, tasteless, and neither acid nor alkaline in its reaction. It swells in water, and does not dissolve readily unless some alkaline salt has been added. It is insoluble in alcohol and ether. Dried *in vacuo*, or at a temperature below 122°, it can be heated to 212° without assuming the insoluble form. The aqueous solution, however, becomes turbid at 140°, coagulates perfectly at 145°, and separates in flakes at 167°. When excessively diluted no change takes place below 194°, and coagula will only separate after long boiling.

Albumen may be precipitated by *dilute alcohol*. *Strong alcohol* coagulates it. *Ether* is said to coagulate the albumen of eggs, but not that of serum. This distinction, however, is not constant. The *oils* do not affect it. *Creasote* and *anilin* coagulate it. Most acids render it insoluble; but, except tribasic phosphoric acid, do not precipitate it, unless added in excess. *Tannic acid* is the only organic acid which precipitates it. It is thrown down by *metallic salts*, but not by *alkalies*.

Albumen is rarely found *isolated* in the economy, being usually in combination with some alkali. Lehmann found that in the albumen of hens' eggs, 1.58 of soda was united with 100 of albumen. This has a slightly alkaline reaction, is more soluble than pure albumen, and coagulates in a white gelatinous mass instead of subsiding in flakes. The alkaline reaction is stronger after boiling than before, showing that a portion of alkali must have been liberated during the process of coagulation. The free alkali combines with a small portion of the albumen to form albuminate of soda, which remains in solution. The albuminate of soda, when saturated with acetic acid, on the application of heat, coagulates in flakes which can be collected, while the ordinary precipitated albumen of the egg passes through the filter and soon clogs its pores.

When this albuminate of soda is treated with dilute alcohol, a

portion is precipitated, free from alkali and poor in salts, while there remains in solution the true albuminate of soda. A farther addition of alkali to normal albumen changes its properties, so that, on the application of heat, there is formed a translucent jelly, containing, according to Lehmann, 4.69 parts of potash, or 3.14 of soda to 100 parts of albumen free from salts. On diluting this solution with water, it no longer yields any precipitate on the application of heat. When treated with excess of alkali, it can be precipitated by any of the acids which do not ordinarily throw down albumen from its solutions. When its solution is boiled, numerous vesicles are formed which adhere closely to the bottom of the vessel; and, on evaporation in the air, it becomes covered with a transparent film of coagulated albumen, so that it has occasionally been mistaken for casein. It yields a perfect flaky coagulum on boiling, after the addition of an alkaline salt, either dry or in the saturated solution.

Acids and *metallic salts* have nearly the same reactions with this variety as with the common albumen. *Organic acids*, added in excess, cause the albumen to remain dissolved on boiling; but the addition of a salt, such as sulphate of soda, chloride of sodium or of ammonium, causes a flaky precipitate. These acid solutions also become covered with a casein-like film on evaporation.

Coagulated albumen possesses the properties already noticed as belonging to the coagulated protein compounds. Albumen loses sulphur in passing from the soluble to the insoluble form. Heated with hydrochloric acid, it assumes a blue color, which inclines more to purple than that of any other protein compound. Boiled for a long time in contact with the atmosphere, it gradually dissolves, forming a non-gelatinizing fluid which contains Mulder's tritoxide of protein. When treated with powerful oxidizing agents, as chromate of potash and sulphuric acid, it yields more acetic acid, benzoic acid, and hydride of benzoyl, and less valerianic acid than the other protein compounds.

The mean result of five analyses by Scherer, the latest analysis by Mulder, which he regards as the most exact, and one of his older analyses are subjoined for the sake of comparison.

	Scherer.	Mulder.	Mulder.
Carbon . . .	54.883	53.5	54.84
Hydrogen . .	7.035	7.	7.09
Nitrogen . .	15.675	15.5	15.83
Oxygen . .		22.	21.23
Sulphur . .	22.365	1.6	.68
Phosphorus . .		0.4	.33
		100.0	100.00

Rüling estimates the albumen of the blood to contain 1.325% of sulphur, that of hens' eggs, 1.748%, while Mulder found 1.3% in the former and 1.6% in the latter. Albumen retains chloride of sodium with such tenacity that it is almost impossible to separate it by washing. Its phosphate of lime usually amounts to 1.6%. From its combination with oxide of lead, Mulder estimated its atomic weight at 22483.9, while from the oxide of silver combination, he calculated it at 22190.2. He supposes the albumen of eggs to be composed of 96.2 protein, 3.2 sulphamide, and .6 phosphamide; and deduces the formula $20(C_{36}H_{25}N_4O_{10}.2HO)+8H_2NS+H_2NP$.

Preparation.—The purest *soluble albumen* is obtained by neutralizing serum or white of egg dissolved in water with acetic acid, and extracting with 20 or 30 times the quantity of distilled water, or with dilute spirit. It is usually prepared by evaporating serum or white of egg in a platinum crucible *in vacuo*, or at a temperature not exceeding 120°, pulverizing the yellow residue, and extracting foreign matters first with ether and then with alcohol.

Coagulated albumen is obtained perfectly pure by washing the precipitate thrown down from white of egg by hydrochloric acid, with dilute hydrochloric acid, and then dissolving the hydrochlorate in water, and precipitating it with carbonate of ammonia. The precipitate is dried, pulverized, and freed from fat by boiling it with alcohol and ether.

Tests.—Albumen is usually known by its coagulation on the application of heat. Several other agents, among which are nitric acid, corrosive sublimate, and chromic acid also coagulate it. The form of the coagulum, as already stated, will indicate

the state in which the albumen exists. At best, however, we can only approximate certainty in our recognition of this substance.

In estimating albumen quantitatively, it is necessary first to neutralize or even slightly acidulate the fluid with acetic acid, taking care to avoid excess of this reagent, before attempting to coagulate it by heat, otherwise it will pass through the filter. It must be thoroughly dried *in vacuo*, also, with the aid of hygroscopic substances, and *cooled* before weighing, or it cannot be estimated with anything like certainty.

Albumen is undoubtedly a most important substance in the building up of the economy. The general opinion among physiologists is that it is transmuted into fibrin, which becomes the true plasma of all the tissues. Lehmann supposes that albumen may be directly converted into tissue, and suggests that the necessary presence of fibrin may be accounted for on the hypothesis that this substance acts as a sort of crystallizing point for the albumen.

FIBRIN.

This substance must be studied in three different modifications: 1. *Soluble* fibrin; 2. *Spontaneously coagulated* fibrin; 3. Fibrin *coagulated by means of heat;* as it has different properties in these three distinct modes of existence.

The *natural solution of fibrin* is the liquor sanguinis of the blood. It is precipitated, along with the albumen, by concentrated solution of potash, but not by acetic acid or caustic ammonia. Ether coagulates fibrin, but not albumen.

Fig. 1.

Fig. 1. Fibrillation of fibrin, as seen by the microscope in inflammatory exudation on the peritoneum.

The most striking peculiarity of fibrin is its property of spontaneous coagulation. In a short time after blood has been drawn, it divides, as

every one knows, into serum and clot. The clot is formed by the spontaneous solidification of the dissolved fibrin, entangling blood-corpuscles in its meshes. The structural arrangement of the clot, or rather the process by which it acquires a definite structure, has been termed the *fibrillation* of the fibrin. When the fresh liquor sanguinis is examined with the microscope, it is found to contain only a few colorless blood-corpuscles. After a time, however, it begins to assume a gelatinous consistence, and then several points or molecular granules make their appearance in different parts of the mass. From these, long fibrils shoot out, crossing one another, forming loops, and interlacing at every possible angle till they have woven a network of fibres.

Many attempts have been made by chemical and physical theorists to account for this remarkable property, but all have totally failed. The chemical change, if any, which fibrin undergoes, in passing from the soluble to the insoluble form, lies entirely beyond the range of our present chemical knowledge. Lehmann objects to the only hypothesis which the physiologists regard as at all tenable, that, namely, which considers this a vital change. He says that, it is at variance with all preconceived ideas of life, to attribute life to a simple organic substance. The objection is somewhat unintelligible, for the cell-membrane can hardly be regarded as anything else than a simple organic substance; and the nucleus envelop has been generally conceded to be pure albumen; yet to both of these vitality is attributed. It matters not whether these notions of cell and nucleus envelops are correct or incorrect; the fact that they are entertained is sufficient to show that it is not an anomaly, as Lehmann would have us believe, in the present state of physiology, to attribute vitality to fibrin.

Spontaneously coagulated fibrin is yellow and opaque, becoming hard and brittle in drying. It is tasteless and inodorous, insoluble in water, merely absorbing that fluid and becoming soft and flexible again. It is insoluble also in alcohol and ether. It decomposes rapidly, and putrefies in the air, dissolving if sufficient water be present, and becoming converted into a substance, which, like albumen, is coagulated by heat. During this process it attracts oxygen and develops ammonia, carbonic acid, butyric acid, and sulphuretted hydrogen, leaving a residue con-

sisting principally of casein and tyrosin. In a saline solution, at a temperature of from 90° to 100°, it forms a viscid solution, having undergone some chemical change. It now coagulates at 164°, and is precipitated by acetic acid, but not by ether.

The fibrin of venous is said to differ from that of arterial blood in this latter reaction. Scherer thinks that the fibrin of arterial or of inflammatory venous blood does not undergo this change. This has been denied, but the question is not yet settled.

Boiled fibrin closely resembles coagulated albumen. Its specific gravity, after deducting for the ash, is 1.2678. It is no longer capable of decomposing peroxide of hydrogen, nor of being converted into an albumen-like substance by digestion in solutions of alkaline salts. Boiled a long time in water, it gives rise to a soluble and an insoluble substance, the teroxide and binoxide of protein of Mulder. Decomposed by oxidating reagents, it yields more butyric acid than any of the protein-compounds, but less acetic and benzoic acids than albumen.

Composition.—Fibrin has never yet been obtained pure, being mixed with white blood-corpuscles, and manifestly containing several organic compounds. The following analyses are the latest that have been published:—

	Scherer.	Mulder.
Carbon	53.571	52.7
Hydrogen	6.895	6.9
Nitrogen	15.720	15.4
Oxygen	22.814	23.5
Sulphur		1.2
Phosphorus		0.3
	100.000	100.0

Dry fibrin contains about 2.6 per cent. of fats combined with ammonia and lime. Mulder found 1.7%, Virchow 0.66% of phosphate of lime in it. It is generally supposed that it contains more oxygen than albumen. Mulder, therefore, regards it as a higher degree of oxidation of protein, combined with sulphamide and phosphamide. His formula for it is $(C_{36}H_{25}N_4O_{11}\cdot 2HO)H_2NS+H_2NP$.

Mulder's *binoxide of protein* is obtained in a variety of ways, among which we may mention the protracted boiling of fibrin in water, with free exposure to the atmosphere, and precipitating with acetic acid. It is a light-yellow, lumpy, tough precipitate, drying to a blackish-green, shining, resinous mass. Mulder's formula is $6(C_{36}H_{25}N_4O_{11}.2HO)+S_2O_2$.

Preparation.—The natural solution of fibrin is obtained by allowing fresh frog's blood to flow into sugared water and filtering off the clear fluid. To obtain spontaneously coagulated fibrin, a blood clot is cut into fine pieces and washed till it is white. Or it may be obtained by whipping coagulating blood with rods or agitating it in a bottle with shot, and then suspending it, in a bag in water, till it is thoroughly washed. Pure boiled fibrin is obtained by drying it, then extracting it with alcohol acidulated with sulphuric acid, and finally with ether.

Tests.—Fibrin is usually recognized by its microscopic characters and by its reaction with alkaline salts. The *quantitative estimation* of this substance is, for the reasons already mentioned, extremely difficult. An approximative estimation is the most that can be made. This is usually accomplished by whipping fresh blood and purifying and drying it, in the manner already described.

Fibrin is found chiefly in the blood, lymph, and chyle. Its proportion varies considerably even in different vessels. Its range is from about 0.2 to 0.3 per cent. in venous blood. The portal vein contains less than the jugular, and the veins remote from the heart generally more than those near it. The blood of new-born infants contains less fibrin than that of adults, the increase of this element being especially conspicuous at the age of puberty. In pregnancy, fibrin increases, particularly during the last three months. Lehmann and Nasse found that the quantity of fibrin was greater during an *animal* than during a *vegetable* diet. According to the latter observer, fibrin is increased during fasting. *Herbivorous* animals are said to have more of this element in their blood than the *carnivorous*, and *birds* more than either.

In disease, rheumatism and inflammation increase it. The quantity of it in the *lymph* of man is stated at 0.052%.

There has been much question recently in reference to the origin of fibrin, but it has been now pretty generally conceded to be formed from albumen. The question also has been asked whether fibrin is the result of a progressive or regressive metamorphosis, *i. e.* whether it is always a stage between albumen and fully developed tissue, according to the old physiological view, or whether it is a step towards decay and elimination. That fibrin is a body of a higher degree of oxidation than albumen is universally admitted; but, as Lehmann urges, it contains less oxygen than the tissues. He is therefore inclined to believe that it is a transition stage, and may on the one side ascend into tissue, or on the other, descend into excretion. In inflammation, he thinks, owing to the diminished supply of oxygen, in consequence of the imperfect action of the lungs, albumen is unable to pass into the higher degrees of oxidation, but is arrested at this lower stage, whence the quantity of fibrin in the blood is necessarily increased. He says: "The frequent but short and incomplete respirations which occur only in febrile (and not in non-febrile) inflammations are only sufficient to convey to the blood sufficient oxygen to convert certain substances into fibrin, but not to oxidate them farther; this is the reason why the amount of fibrin attains its maximum in pneumonia and pleuritis, and why the blood in the former disease is most rich in carbonic acid, for this gas is scantily excreted in proportion as oxygen is scantily received in the lungs."

Muscular fibrin has been recently shown to be a different substance from the true, or blood fibrin just described. It is precipitated from the hydrochloric solution of flesh, by neutralization, as a coherent, elastic, snow-white mass, which may be detached in membranes, and presents under the microscope, when tension is used, characters analogous to those of blood fibrin. Chloride of calcium and sulphate of magnesia precipitate it only after boiling. Nitric acid and chromic acid throw it down, while hydrochloric acid in excess only clouds its alkaline solution. Uncoagulated *syntonin*, as this substance is now called, is insoluble in nitre. Besides all these peculiarities, it differs slightly from fibrin in chemical composition.

GLOBULIN.

This substance, which has also received the name of *crystallin*, occurs naturally in the soluble state, but becomes insoluble by boiling. The *soluble* form, dried at 120°, is yellowish, transparent, and easily reduced to a snow-white powder. It is tasteless and inodorous, swells in water, like albumen, and gradually dissolves. It is precipitated by alcohol, and then is insoluble in water, but partially soluble in boiling alcohol. It is distinguished from albumen by its solution not becoming opalescent at a lower temperature than 164°. At 182° it becomes milky, and at 199° separates as a globular mass or as a milky coagulum. It is not precipitated by acetic acid or by ammonia; but, when treated with one of these reagents and neutralized with the other, it becomes turbid. It decomposes more readily than the other protein compounds, and when boiled, it develops ammonia.

Composition.—Globulin from the crystalline lens gave the following results to Mulder and Rüling:—

	Mulder.	Rüling.
Carbon	54.5	54.2
Hydrogen	6.9	7.1
Nitrogen	16.5	37.5
Oxygen	22.1	
Sulphur		1.2
	100.0	100.0

Berzelius supposed globulin to contain phosphorus. Mulder found none, but only sulphur in the proportion of 0.265%. Lehmann makes it 1.134%, and Rüling 1.227%.

It is prepared by neutralizing the fluid of the crystalline lens with acetic acid, evaporating to dryness at a temperature not exceeding 120°, and extracting with ether and dilute alcohol. Coagulated globulin is procured by extracting the precipitate obtained by boiling with water, alcohol, and ether, and by precipitating with hydrochloric acid and washing thoroughly.

In the cells of the crystalline lens is a fluid which contains 35.9% of dry globulin. It is also one of the principal con-

stituents of the blood, forming, with hematin, the viscid fluid contained in the red corpuscles.

It is thought to be formed by the action of the walls of the corpuscles upon the albumen of the blood, and seems to be albumen modified by oxidation, and to hold an intermediate place between this substance and fibrin. It has been supposed by some to be directly converted into fibrin, but of this there can be no certainty in the present state of chemical science.

The use of globulin in the crystalline lens is to attain an achromatic apparatus, by introducing a substance of different refracting power from the membranous portion of the lens. It is also worthy of note that nature has not relied alone upon the anatomical structure of the lens, but has increased the *density* of the globulin itself from the surface to the centre of this organ. Thus a lens weighing 30 grains, taken from the eye of an ox, had a specific gravity of 1.0765, while the centre, weighing 6 grains, was 1.194. This globulin is separated, entirely free from hematin, from the blood of the minute capsular artery by the lens.

The use of globulin in the blood-corpuscles is entirely unknown.

CASEIN.

Soluble casein when dry is an amber-yellow, inodorous, insipid, viscous mass, neither acid nor alkaline. It dissolves in water to a yellowish, viscid fluid, which, on evaporation, is covered by a white film of insoluble casein. Exposed to the air, it putrefies, developing ammonia, leucin, tyrosin, &c.

Alcohol renders casein opaque, and dissolves a small portion of it, which may be obtained in an unchanged state by evaporation. Boiling alcohol dissolves more of it, but lets it fall on cooling. This reagent precipitates casein from a concentrated aqueous solution, but the precipitate retains its solubility in water, unless a large quantity of strong alcohol has been added.

Boiling does not coagulate casein from its solutions. Acids throw it down and partially combine with it, but on neutralization with alkalies it again dissolves, and the precipitate is solu-

ble in both pure water and alcohol. It is distinguished from albumen by the fact that *acetic* and *lactic* acids precipitate it. Alcohol dissolves its precipitates, and the alcoholic solution cannot, of course, be precipitated by acids. *Tannic acid* throws it down from all solutions. Its products of decomposition are the same as those of albumen and fibrin. The *alkaline earths* and their *salts on the application of heat* precipitate it. *Metallic salts* throw it down, and form with it two sets of compounds, one containing the acid, the other the base.

When obtained free from alkalies, its reactions are somewhat different. It is very slightly soluble in water, and not at all in alcohol. It reddens blue litmus paper, and forms solutions with carbonate and phosphate of soda, which no longer exhibit an alkaline reaction. It dissolves in many neutral alkaline salts, does not coagulate on boiling, but forms the film already described. It dissolves in dilute mineral acids, but is precipitated by excess of these reagents, and, on evaporation, the acid solution is covered with the same precipitate in the form of a colorless, transparent, and toughish membrane. Heat alone does not coagulate casein, but if carbonate of potash or nitre with a little potash be added, and the solution neutralized, a copious thick coagulum is formed when the solution is boiled.

Casein is coagulated by exposure to the air and by the action of rennet, the mucous membrane of the calf's stomach. In the first instance, it is precipitated by the lactic acid, formed by the action of the air on the sugar of the milk. In the latter case, Simon and Liebig supposed that the rennet acted as a ferment, hastening this same oxidation. Selmi's experiments are opposed to this view; showing, as they do, that the alkaline reaction remains after the coagulation has taken place, so that the cause of this change is still enveloped in obscurity. Scherer's experiments show that it cannot take place without the presence of oxygen.

The researches of Mulder and Schlossberger have rendered it probable that this substance is composed of several distinct bodies.

Coagulated casein is hard, yellowish, and translucent. It swells, but does not dissolve in water, and is insoluble in alcohol.

It combines with acids and alkalies, and resembles coagulated albumen in its relations to the mineral acids. When *heated*, it softens, becomes ductile and elastic, and at a higher temperature it fuses, carbonizes, and gives off the same substances as albumen and fibrin under similar circumstances. During putrefaction, it develops first carbonate and hydrosulphate of ammonia, and then valerianic and butyric acids, leucin, a white, crystallizable, sublimable body, having a strong fecal odor, and an acid, which, when decomposed with a mineral acid, yields a brown substance, tyrosin and ammonia.

The coagulum obtained from *woman's* milk, differs from that of *cow's* milk in being soluble in water, loose, and jelly-like, and deliquescent. Lehmann thinks that these differences depend upon the greater alkalinity of woman's milk.

Composition.—The following analyses of casein are from

	Mulder,	Scherer, and Dumas.	
Carbon . . .	53.83	54.665	53.7
Hydrogen . .	7.15	7.465	7.2
Nitrogen . .	15.65	15.724	16.6
Oxygen } Sulphur } . .	23.37	22.146	22.5
	100.00	100.000	100.0

Recent investigations establish the percentage of sulphur in purified casein at 0.85. Casein that has not been treated with acids contains about 6% of phosphate of lime.

Mulder regards this substance as a compound of protein and sulphamide, but has abandoned his old formulæ, and proposed no new one, because of the uncertainty still existing in regard to its being a simple substance.

Preparation.—Soluble casein is obtained in a variety of ways. We shall only cite Rochleder's method of procuring it free from alkali.

Skimmed milk is coagulated with dilute sulphuric acid, the precipitate pressed and dissolved in a solution of carbonate of soda. This solution is allowed to stand for some time in a shallow vessel, and the fat that forms on the surface is skimmed off

with a spoon, or the subjacent fluid is decanted by means of a siphon. This solution is again precipitated with an acid, and subjected to the same treatment. After this process has been gone through three times, the remainder of the fat is extracted with alcohol and ether. Repeated boiling in water entirely separates all the acid, and casein is obtained in its purest possible form.

Tests.—Recent examinations have shown that the old tests for casein, its conversion into a pellicle, its precipitability by acetic acid, &c., must be abandoned, as they are not at all diagnostic.

When *rennet* is used, it is necessary first, that it should be fresh; and then, that it should be digested in the fluid at a temperature of 104° for not longer than two hours. Should no coagulum then be formed, casein is probably absent.

Lehmann's method is first to add hydrochlorate of ammonia, in order to get rid of albuminate of soda; to filter; then to add sulphate of magnesia and chloride of calcium; to filter again, if a precipitate falls from the cold solution; then to boil it, and, if a precipitate form, to determine its nature by rennet.

The best quantitative process, according to Lehmann, is that proposed by Haidlen. He stirs milk with one-fifth of its weight of finely pulverized gypsum, heats it to 212°, and removes the fat, milk-sugar, and most of the salts by means of ether and alcohol. The residue is not pure casein, but the quantity of that ingredient is easily ascertained, by determining the proportion of fat, sugar, and salts contained in the milk.

Physiological Relations.—Casein occurs in the milk of all the mammalia. In women's milk, of good quality, Haidlen found 3.1%; in inferior milk only 2.7%. In cow's milk, the proportion has been variously computed, at from 3% to 7%; in asses' milk, at from 1.95% to 2.3%; and in goat's milk, at from 4.52% to 9.66%. According to Dumas and Bensch, an *animal* diet increases the quantity of casein.

It is found partly in solution and partly in the wall of the milk-globules. The presence of an investing membrane around the milk-globules is beautifully shown by an experiment devised by Mitscherlich. On shaking *fresh* milk with ether, scarcely

any fat is taken up, but on adding some substance capable of destroying cell-walls a great quantity of fat, all indeed that the milk contains, will be dissolved by the ether. The microscope shows that milk-globules, acted on by ether without the addition of caustic alkali, become opaque, corrugated, and transparent, showing that the ether has coagulated the cell-wall. Sulphate of soda bursts the capsule of the globules, and allows the ether to get free access to the contained fat, and the microscope then discovers minute granules, the fragments of the broken up corpuscles floating in the fluid. "Hence," says Lehmann, "we perceive that our ordinary casein not only contains the protein-compound dissolved in the milk, but likewise another, which forms the capsule of the milk-corpuscles, so that we thus also have a microscopico-mechanical proof of the composite nature of ordinary casein."

The origin of casein is entirely unknown. It probably exists in the blood, and is only eliminated from it by the mammary glands. Its relations to albumen have not been determined.

"The occurrence of casein in the milk, the best of all kinds of food, leaves no doubt regarding the uses of this substance, especially since we see how nature provides that more casein is always supplied for the building of the bodies of very young animals than is required for their future support. Casein not only yields to the infant body the material by which soft parts are nourished and caused to grow, but likewise conveys into the system a sufficient quantity of bone-earth and lime to cause the skeleton of the infant body gradually to attain its necessary solidity."*

There are vegetable substances intimately related to this protein group, of great consequence as nutritive substances, which shall now be glanced at.

GLUTEN.

When dried, this substance is transparent, hard, and difficult to pulverize. When moist, it is adhesive, viscid, and elastic. It

* Lehmann's Physiological Chemistry.

is insoluble in cold, and but slightly soluble in hot water; easily soluble in boiling alcohol, from which it is precipitated by water, by corrosive sublimate, and by acetate of lead. It does not dissolve readily in acetic acid, but in other respects possesses all the properties of protein compounds.

Composition.—Analyses of this compound vary greatly. We copy those of

		Scherer, and Mulder.
Carbon	54.6	54.84
Hydrogen	7.4	7.05
Nitrogen	15.8	15.71
Oxygen }	22.2	21.80
Sulphur }		0.60
	100.0	100.00

Rüling found 1.134% of sulphur in wheat-gluten, and Verdeil 0.985% in rye-gluten.

Preparation.—It is obtained by kneading flour under water, boiling the residue with alcohol to extract starch, filtering while hot, and cooling and evaporating the solution, when it is precipitated in white flocculi.

LEGUMIN.

This substance forms either a nacreous, iridescent precipitate, or falls in flocculi. When dried, it is yellow, transparent, and brittle. It coagulates, like albumen, from its aqueous solution, but is precipitated, like casein, by acetic and phosphoric acids. It does not, however, dissolve in concentrated acetic acid. It is coagulated by rennet. It dissolves readily in ammonia and the other alkalies.

Composition.—The analyses of this substance vary so much that it is evidently an impure preparation which has been analyzed. The following are the results obtained by

	Dumas and Cahours, and Rochleder.	
Carbon	50.50	56.24
Hydrogen	6.78	7.97
Nitrogen	18.17	15.83
Oxygen } Sulphur }	24.55	19.96
	100.00	100.00

Preparation.—Legumin is found in peas and beans, and is obtained by making a watery extract of these seeds. This extract is acid, and on neutralization, the legumin is precipitated. It is purified by solution in ammonia, precipitation by an acid, and digestion in alcohol and ether.

TEROXIDE OF PROTEIN.

This is a brittle substance when dry; but, in a moist state, it is tough, viscid, and ductile. When warmed, it smells like gelatin. It is soluble in water, but insoluble in alcohol and ether. It is precipitated by dilute mineral acids, chlorine, tannic acid, corrosive sublimate, salts of lead, silver, zinc, and iron, but not by ferrocyanide of potassium, the alkaline salts, or chloride of barium. With alkalies it forms neutral compounds, from which it is precipitated by metallic salts. Boiled with caustic potash, it develops ammonia, and is converted into a substance which, according to Mulder, is a true teroxide of protein ($C_{36}H_{25}N_4O_{10}$ + 3O + 3HO).

Composition.—Mulder supposes this substance to be a combination of the true teroxide of protein with ammonia, and gives the formula $H_4NO + 2(C_{36}H_{25}N_4O_{13}) + 3HO$.

Tests.—These are not yet fully determined upon.

Physiological Relations.—It exists, according to Mulder, in normal blood and in pus, as well as in all fluid exudations. Its quantity in the blood is increased in inflammatory disease. He regards the *pyin* of Güterbock as identical with this compound. "If," says Lehmann, "more accurate investigations confirm the existence of this teroxide of protein in the manner that Mulder supposes, we shall then acquire a knowledge of an important

intermediate link in the metamorphosis of the animal tissues; and, in particular, we shall have considerably approximated to the yet unsolved problem of the conversion of albuminous bodies into bodies yielding gelatin, or of fibrin into tissue."

CHAPTER IV.

THE GELATINOUS GROUP.

GELATIN does not exist ready formed in the organism, but is produced by boiling certain parts with water. It is distinguished from other animal substances by its property of swelling and becoming translucent in cold water and dissolving in hot; and by its reaction with chlorine, tannic acid, and the metallic and earthy salts.

There are two prominent varieties of gelatin, *bone-gelatin*, *glue* or *glutin*, and *cartilage-gelatin* or *chondrin*.

GLUTIN.

Pure glutin occurs in colorless, transparent pieces, which are hard, horny, brittle, inodorous, insipid, heavier than water, and which do not stick to the pestle like the protein compounds, when triturated.

In cold water it softens, in warm water it forms a viscid solution which cools to a jelly. After repeated solution in hot water, it no longer gelatinizes on cooling. Gelatinized glutin becomes acid on exposure to the air, and loses its tenacity. It is insoluble in alcohol, ether, fats, and volatile oils.

Acids, with the exception of the *tannic*, do not precipitate it. *Alkalies* only throw down a little bone-earth, which is often mixed with it. The only *metallic salts* which precipitate it are the bichloride and sulphate of the binoxide of platinum, corrosive sublimate, and the basic sulphate of binoxide of iron. The latter throws down a bulky precipitate, which becomes deep red

by drying. *Ferrocyanide of potassium* does not affect its solution. *Chlorine* separates a thready coagulum. *Creasote* renders the solution milky.

Dry gelatin, when *heated*, swells up, emits the odor of burned horn, does not catch fire easily, burns for but a short time, and leaves a voluminous, blistered, shining coal.

Boiled with concentrated *nitric acid*, it is converted into oxalic and saccharic acids, and into two substances resembling suet and tannic acid. With *sulphuric acid*, it forms a solution which, on boiling, yields leucine, glycine, &c. With *chromic acid*, it furnishes most of the non-nitrogenous acids, with nitriles and aldehydes. Boiled with hydrated potash, it develops ammonia, and is decomposed into leucine and glycine.

Composition.—Glutin yields according to

	Mulder,	and Scherer.
Carbon	50.40	50.76
Hydrogen	6.64	7.15
Nitrogen	18.34	18.32
Oxygen	24.62	23.77
	100.00	100.00

Mulder's formula is $C_{13}H_{10}N_2O_5$; Liebig's $C_{52}H_{40}N_8O_{20}$. Schleifer found from 0.12 to 0.14 per cent. of sulphur in glutin from bones and ivory.

Preparation.—Berzelius obtained glutin from common glue, by softening it in water, subjecting it repeatedly to strong pressure, suspending it in a bag in cold water till everything soluble was taken up, and then heating it to 122°. The solution thus obtained was rapidly filtered while still hot. Pure glutin can only be obtained from cellular tissue, shavings of hartshorn, calves' feet, and the swimming bladder of certain fishes. These are boiled till they are thoroughly dissolved, filtered whilst still hot, and the resulting impure glutin treated according to the method of Berzelius just described.

Combinations.—When chlorine gas is passed through a solution of glutin, each bubble of gas is enveloped in a glutinous capsule; the fluid becomes milky; white flakes appear; and at

the bottom of the vessel is deposited a semitransparent jelly. The white substance is a chlorite of glutin.

The action of *acids* on glutin is imperfectly known. With dilute mineral acids, it forms combinations, which, on cooling, behave like pure glutin. Concentrated *acetic acid* dissolves glutin which has been softened in water, and deprives it of its property of gelatinizing on cooling. The precipitate with tannic acid, according to Mulder, consists of three equivalents of glutin and two of tannic acid $= C_{39}H_{30}N_6O_{15} + C_{36}H_{14}O_{32}$.

Glutin combines with several basic salts. A very considerable quantity of bone-earth dissolves in a solution of glutin. Treated with alum and with sulphate of the peroxide of iron, glutin yields a precipitate after the addition of an alkali.

Physiological Relations.—Glutin is obtained from bones, tendons, skin, and permanent cartilages when they become ossified from disease. The conversion of the basis of these parts into glutin goes on without any evolution of gas or other signs of chemical action, and seems to consist only of a change of molecular constitution.

Gelatin is thus an essential part of the passive and protective parts of the organism, and does not enter into the formation of its active parts.

CHONDRIN.

When dry, chondrin is a transparent, horny, glistening mass, more colorless than glutin, from which it differs in its reactions with acids and the metallic salts. The former and many of the latter precipitate it. Salts of alumina throw down white, compact flocks, which, on drying, cake together; they are insoluble in water, but dissolve in excess of the earthy salt, as well as in chloride of sodium, and the alkaline acetates.

Composition.—It contains according to

	Mulder.	Scherer.
Carbon	49.97	50.754
Hydrogen	6.63	6.904
Nitrogen	14.44	14.692
Oxygen	28.59	27.650
Sulphur	0.38	
	100.00	100.000

Mulder's formula is $C_{32}H_{26}N_4O_{14}$; Scherer's, $C_{48}H_{40}N_6O_{20}$.

Preparation.—Chondrin is obtained by boiling the permanent cartilages in water, for eighteen or twenty-four hours. It is purified in the same manner as glutin, and the dried residue is extracted with alcohol.

Physiological Relations.—It is found in all healthy permanent cartilages, and in the temporary cartilages before ossification. Sometimes it is found in diseased bone. It is probable that glutin is formed from it.

There are other varieties of gelatin different from these two; that, namely, which is obtained from bone altered by osteomalacia, and that which is procured from the elastic coat of arteries.

CHAPTER V.

NITROGENOUS BASIC BODIES.

THERE are obtained from the animal body many nitrogenous substances which are not histogenetic, that is, which have no share in the process of nutrition or the construction of tissues. Most of them, nevertheless, are important to the well-being of the creature, because they form essential constituents of secretions, or constitute intermediate stages between the tissues and the excretions.

These substances are true alkaloids capable of forming salts with acids. Many of them have sufficiently powerful basic properties to precipitate the heavy metals from their salts, and even to liberate ammonia.

They are divided into two very natural groups, the non-oxygenous and the oxygenous alkaloids.

The bodies of the first class do not exist as such in the human body, but are obtained by the destructive distillation of the gelatinous tissues. There are three of them obtained from these tissues; *aniline*, *picoline*, and *petinine*. They are highly refract-

ing, colorless fluids, pungent in their smell and taste. They have no physiological interest.

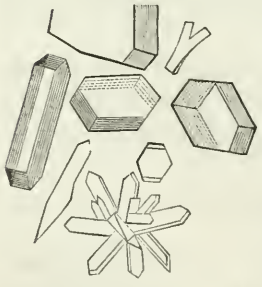
The *oxygenous alkaloids* are more interesting. Many of them exist already in the economy, and nearly all of them throw some light upon those vital processes which lie beyond the range of ordinary research. Their basicity varies greatly, and no direct relation has yet been detected between their atomic constitution and their saturating capacity. They are nearly all crystallizable, inodorous, soluble in alcohol, and usually bitter in taste.

CREATINE.

When finely chopped flesh is thoroughly kneaded in water, and subjected to powerful pressure, a liquid is obtained which contains salts and several animal substances. Coagulable matters being removed by boiling and the phosphates by caustic baryta, the fluid is to be evaporated to one-twentieth of its bulk, care being taken to remove the pellicle which forms from time to time upon the surface. Being now allowed to stand, a copious deposit of crystalline needles is obtained. These, when separated from the mother-liquor by a filter, washed with alcohol and cold water, and then purified by crystallization from hot water, are pure *creatine*.

The crystals of creatine are transparent, very brilliant, belong to the clinorhombic system, and contain two atoms of water. It is bitter, pungent, and irritates the pharynx when swallowed. At 212° it loses its water, and at a higher heat is decomposed. It dissolves in 74.4 parts of cold water, but in much less boiling water. It requires 9410 parts of alcohol to dissolve it, and is insoluble in ether. Boiled with baryta water, it is decomposed into ammonia and carbonic acid, or into *urea* and *sarcosine*.

Fig. 2.



Creatine, prepared from beef and crystallized from hot water.

The formula of the anhydrous substance is $C_8H_9N_3O_4$, and its atomic weight is 1637.5.

Creatine is a constant constituent of muscular flesh, though found in very small quantity. The proportion varies in different animals. In man, Schlossberger estimates it at 0.067% of muscle. It is not to be found in the substance of the brain, the liver, or the kidneys. It is also found very constantly in the *urine*.

The following is Liebig's method of procuring it from this fluid. The urine is treated with lime-water and chloride of calcium, filtered, evaporated, and crystallized to remove the salts. The mother-liquor is decomposed with one-twenty-fourth of its weight of a syrupy solution of chloride of zinc. After some days, roundish granules of a compound of chloride of zinc with creatinine, mixed with some creatine, separate. These granules are dissolved in boiling water, and the solution treated with hydrated oxide of lead till the reaction becomes alkaline. The filtered fluid is treated with animal charcoal and evaporated to dryness. Boiling alcohol dissolves the creatine and leaves the creatinine.

It was at one time supposed that creatine was the result of a progressive metamorphosis, and, therefore, a nutritive substance. Liebig's researches, however, have clearly proved it to be a *product of excretion*. It is probably an intermediate stage between muscular tissue and urea.

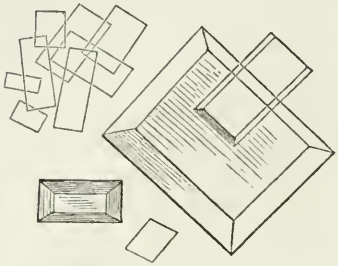
CREATININE.

The method of obtaining this body from urine has already been mentioned. It is more easily obtained by mixing creatine with hydrochloric acid, evaporating till all excess of acid has passed off, and digesting with hydrated oxide of lead, to decompose the hydrochlorate thus formed.

It forms colorless, very glistening crystals belonging to the monoclinometric system; has a caustic, burning taste; is soluble in 11.5 parts of water at ordinary temperatures, in less hot water, in 100 parts of cold spirit of wine, and very freely in hot alcohol. It is slightly soluble in ether. It is precipitated in crystals by nitrate of silver, corrosive sublimate, and chloride of zinc. Bichloride of platinum gives no precipitate in a dilute solution.

According to Liebig, its formula is $C_8H_7N_3O_2$, and its atomic weight, 1412.5.

Fig. 3.



Creatinine.

Liebig has only found this substance in *flesh* and *urine*. Its proportion is unknown, but there is less of it than of creatine. Scherer's researches have rendered it probable that the *liquor amnii* contains creatinine.

It is probably formed from creatine. These substances are found in inverse ratio in muscles and urine; and the latter fluid, when putrid, yields no creatine, but only creatinine. It is, therefore, apparently, another step in the regressive metamorphosis.

TYROSINE.

When cheese, freed from butter, is fused with hydrate of potash till hydrogen is given off, or till the brown tint has passed into a yellow, tyrosine is formed at the expense of the casein. On dissolving in hot water and treating with acetic acid, the tyrosine separates in needles, which are purified by solution in potash water and a second acidulation with acetic acid.

It forms silky, glistening, dazzlingly white needles, of difficult solubility in water, and altogether insoluble in alcohol and ether. It dissolves readily in alkalies, and combines with acids, except the acetic.

Liebig's formula is $C_{16}H_9NO_5$, but he thinks it needs revision.

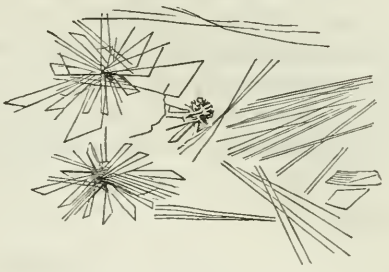
Tyrosine is formed during the putrefaction of albumen, fibrin, and casein.

LEUCINE.

The mother-liquor, remaining after the separation of tyrosine from casein fused with potash, contains leucine, which crystallizes from it, and is easily purified by recrystallization from alcohol.

It occurs in glistening, colorless leaves, which cranch beneath the teeth, and convey to them the sensation of a fatty matter. It is tasteless and inodorous; fuses above 212°; sublimes unchanged when carefully heated to 338°; is soluble in 27.7 parts of water at 63°, in 625 parts of alcohol of 0.828, and in much smaller quantities of hot water and alcohol. It is insoluble in ether. Proto-nitrate of mercury is the only reagent which precipitates it from its watery solution. It dissolves more readily in ammoniacal than in pure water. It dissolves unchanged in cold hydrochloric and sulphuric acids, and the solution may be warmed without the occurrence of decomposition; it also dissolves unchanged in cold nitric acid, but on boiling it is volatilized. When oxidated, nitrogen is given off and *leucic acid* ($C_{12}H_{11}O_5HO$) is formed. Fused with hydrated potash, carbonic acid, hydrogen, and valerianate of ammonia are simultaneously formed.

Fig. 4.



Leucine.

Mulder's formula is $C_{12}H_{12}NO_4$. Recent investigations, however, by a number of observers, have established the formula $C_{12}H_{13}NO_4$. Its atomic weight is 1637.5.

Leucine combines with acids to form beautifully crystallizable salts.

It may be obtained from gelatin, as well as from albuminous substances, by fusing with hydrated potash. It is also procured from flesh by warming it with concentrated sulphuric acid.

SARCOSINE.

This substance is obtained as a result of the decomposition of creatine, and does not occur ready formed in the animal body. A boiling, saturated solution of one part of creatine is digested with ten parts of pure, crystallized, caustic baryta; and, after

ammonia ceases to be given off, the carbonate of baryta is filtered off, and sarcosine allowed to crystallize from the liquid.

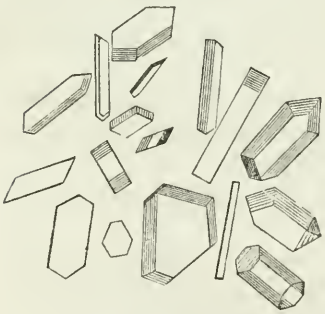
It occurs in broad, colorless, transparent plates or right rhombic prisms, acuminated on the ends, melting at 212°, and subliming unchanged at a higher temperature. It is very soluble in water, sparingly so in alcohol, and not at all in ether. It has a sharp, sweetish, faintly metallic taste, and with salts of copper gives the same fine blue tint as ammonia.

Its formula, according to Liebig, is $C_6H_7NO_3$, its atomic weight 1012.5.

GLYCINE.

This substance, also known as *sugar of gelatin* and *glycocoll*, is obtained as a result of the decomposition of gelatin by the concentrated mineral acids or the caustic alkalies. If gelatin be boiled with a strong solution of potash, it is entirely resolved into four parts of glycine and one of leucine. The fluid, neutralized with sulphuric acid, is evaporated to dryness, and the residue extracted with alcohol, which dissolves both alkaloids. The glycine, being less soluble than the leucine, crystallizes first, and is purified by recrystallization and treatment with animal charcoal.

Fig. 5.



Glycine.

Its crystals are colorless, rhombic prisms, cranching between the teeth, inodorous, sweet, but not so much so as cane-sugar. They dissolve in 4.3 parts of cold water, and with more difficulty in cold, but more easily in hot alcohol. They are insoluble in ether, and have no effect on vegetable colors. Sulphate of copper and potash form with it a blue solution, which, when heated, lets fall no suboxide of copper. Boiled with hydrated baryta or oxide of lead, it gives off ammonia, and assumes a fiery-red tint, which passes off on the prolonged application of heat.

The formula of glycine dried at 212° is $C_4H_5NO_3$, its atomic weight, 937.5.

Glycine forms crystallizable compounds with acids, salts, and bases.

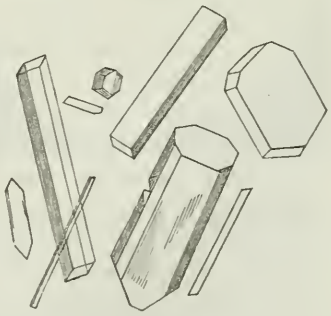
It has not yet been found in an isolated state in the body, but it is supposed to exist there, in combination with animal acids, from which it is separated by the process already described. Taken into the system, it increases the amount of urea and uric acid, but is not found unchanged in the urine.

UREA.

This substance exists in the urine, and may be obtained from it by evaporating to dryness, extracting the residue with alcohol, precipitating the urea as a nitrate by means of nitric acid, decomposing the salt with carbonate of lead or baryta, separating these by crystallization or by hydrosulphuric acid, evaporating and crystallizing.

It is also obtained by mixing twenty-eight parts of anhydrous ferrocyanide of potassium with fourteen parts of well-dried, good peroxide of manganese, and heating to redness. It is then extracted with cold water and mixed with twenty and a half parts of dry sulphate of ammonia. Sulphate of potash separates, and the cyanate of ammonia, now converted into urea, remains in solution.

Fig. 6.



Urea.

It crystallizes in white, silky, glistening needles, or flat, colorless, four-sided prisms, full of cavities, and apparently made up of numerous parallel, crystalline lamellæ; the ends being terminated by one or two oblique surfaces. It is devoid of smell, has a cooling, saltish taste, and is unaffected by exposure to the atmosphere. It dissolves readily in its own weight of water, with evolution of heat; and in every pro-

portion of hot water. It is soluble in four or five parts of cold and two parts of hot alcohol, but insoluble in pure ether and ethereal oil. It has no action on vegetable colors. Its *concentrated* aqueous solution is not changed by boiling or by long keeping, but a dilute solution suffers change. At about 250° it fuses without change; a little above that temperature it begins to develop ammonia, and is converted into cyanuric acid, which passes, by being rapidly heated, into cyanic acid. When kept in fusion some time at from 300° to 340°, *biuret* is formed in addition to the above-named compounds.

Urea combines only with certain acids and with but a few bases. Neither the metallic salts, tannic acid, nor any other reagent can precipitate it from its solutions. Nitrous acid decomposes it into nitrogen, water, and carbonic acid; chlorine, into nitrogen, carbonic, and hydrochloric acids. Boiled either with strong mineral acids or with caustic alkalies, it takes up two atoms of water, and is decomposed into ammonia and carbonic acid. The same change takes place, when putrefying or putrifiable organic matter is introduced into solutions of urea.

The formula of urea is $C_2H_4N_2O_2$, its atomic weight 750. Dumas thought it an amide of carbonic acid; Berzelius, an ammonia conjugated with a nitrogenous body which he calls *urenoxide;* an idea which Lehmann thinks is fully borne out by its reactions.

There are but three salts of urea, the *hydrochlorate*, the *nitrate*, and the *oxalate*.

The *hydrochlorate* is white and hard, crystallizing in plates which deliquesce, and are gradually decomposed by the action of the atmosphere.

The *nitrate* separates, on mixing nitric acid in excess with a concentrated solution of urea, in large, nacreous, shining scales, or in small, glistening, white plates. It is unalterable by the atmosphere, is acid in its taste, more soluble in pure water than in water containing nitric acid, soluble in alcohol, with great depression of temperature. It rendens litmus, decrepitates on being heated, but when its temperature is slowly raised to 284° it is decomposed into carbonic acid, nitrous acid, urea, and nitrate

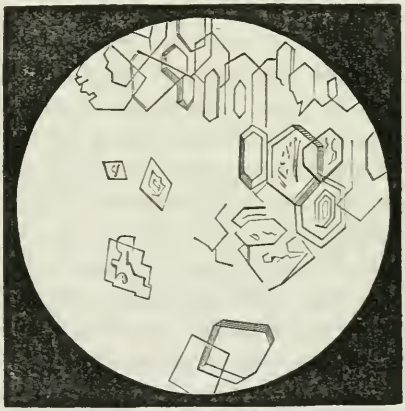
of ammonia. From a solution not too dilute, oxalic acid precipitates oxalate of urea.

Oxalate of urea may be obtained by direct union of the two elements. It forms long thin plates or prisms, and under the microscope usually appears in hexagonal plates, similar to those of nitrate of urea, intermingled with four-sided prisms.

In testing albuminous fluids for urea, it is first necessary thoroughly to coagulate the protein compounds, by acidulating with acetic acid before boiling. The remaining fluid is extracted with cold alcohol, and rapidly evaporated till the chloride of sodium crystallizes out as completely as possible. Then, on bringing a drop of the mother-water in contact with nitric acid under the microscope, rhombic octahedra and hexagonal tablets make their appearance. If the angles of these crystals are found to measure 82°, the presence of urea is rendered certain.

Mitscherlich estimated the quantity of this salt by converting it into *nitrate of urea*, and weighing as such. This is subject to many errors. To obtain a tolerably correct result, it is necessary to use an excess of nitric acid, to lower the temperature artificially, and allow the precipitate to cool some time before filtering, to rinse the salt with cold nitric acid, to press it, and to dry in a temperature not exceeding 230°. The method by *sulphuric acid* is much more exact. The amount of potash and ammonia in the sample of urine having first been determined, a second specimen is treated with sulphuric acid, and heated to 360° or 390° as long as any effervescence occurs; the fluid is then filtered, and the ammonia estimated as ammonio-chloride of platinum. From this it is easy to calculate the amount of urea.

Fig. 7.



Nitrate of Urea.

Millon's method is based upon the fact that nitrous acid decomposes urea into nitrogen and carbonic acid. To effect this, nitrite of suboxide of mercury is dissolved in nitric acid, and added to a weighed portion of urine. When this is warmed, nitrogen and carbonic acid escape, and the latter being fixed in a potash-bulb, is weighed. It must always be remembered that free carbonic acid has been shown to exist in the urine.

Bunsen has proposed a method based on the fact that, *in closed vessels*, solutions of urea *undergo decomposition at a temperature from* 250° to 460°. The carbonic acid thus formed is combined with baryta, weighed, and the urea calculated from it.

Physiological Relations.—Urea, being one of the chief products of renal excretion, occurs chiefly in the urine. Its proportion to the entire secretion varies greatly, in consequence of the variable amount of water contained in urine. As a general thing, however, it constitutes from 2.5 to 3.2% of the entire secretion. Its ratio to the other solid constituents is about 9 : 11 or 7 : 9; and a healthy man, in twenty-four hours, excretes from 340 to 416 grains.

Lehmann has shown that the excretion of urine depends very much on the nature of the diet. Thus, his own natural evacuation of urea, with a mixed diet, being 32.5 grammes (401.6 grains); he excreted, on a purely animal diet, 53.2 grammes; on a purely vegetable one, 22.5 grammes; and on a non-nitrogenous diet, 15.4 grammes. This excretion goes on even while fasting. Lassaigne found urea in the urine of a madman who had fasted fourteen days, and Lehmann found 1% of it in his own urine after living three days on non-nitrogenous food.

Strong muscular *exercise* increases its quantity. Lehmann found his own urea increased from 32 to 37 grammes by it. Women, according to Becquerel, secrete less than men in the proportion of 15.6 to 17.6.

Urea is found in the blood, especially in Bright's disease. It has also been detected in milk, bile, saliva, and dropsical effusions.

The difficulty of detecting urea in the blood led the old physiologists to suppose that it was formed in the kidneys, and that when it occurred in the blood it was in consequence of resorp-

tion. It was found, however, that it existed in large quantities when the kidneys were extirpated, and that the imperfection of our analytical methods is so great that it is impossible to detect quite a large quantity of this substance dissolved in blood. If, then, we consider that it is swept out by the kidneys as fast as it is formed, we shall not be surprised at the impossibility of detecting it, at present, in healthy blood.

Supposing it to exist in blood, the next question is, whether it is *formed* there or in the muscles. Liebig, in his extensive researches on muscular fluids, could detect no urea in them, though he found substances from which it could be artificially produced. It is therefore probable that it is formed in the blood from substances taken up from the muscles, in consequence of the action of the free oxygen and alkali contained in that fluid upon them. Among these, creatine and inosic acid probably play a very important part. The excess of nitrogenous food is also most likely converted into urea in the blood.

XANTHINE.

When carbonic acid is passed through the potash solution of certain urinary calculi, there falls a white powder, which is neither crystalline nor gelatinous. When dried, it forms pale yellowish, hard masses, which, when rubbed, assume a waxy brightness. It is very slightly soluble in water, insoluble in alcohol and ether, and when heated decomposes without fusion. It dissolves in ammonia; but, on evaporation, loses the greater part of the alkali, and separates as a yellowish, foliaceous mass. It dissolves freely in the caustic alkalies, from which carbonic acid separates it. It dissolves in nitric acid without development of gas, and in sulphuric acid, to which it communicates a yellow color. It is nearly insoluble in hydrochloric and oxalic acids, and forms no definite compounds with acids, alkalies, or salts.

Its formula has been calculated at $C_5H_2N_2O_2$. It has been regarded as uric acid in a lower state of oxidation, but nothing definite is known about it.

It has been rarely found in the human body, and then in animal calculi. Scherer has discovered a substance which he

calls *hypoxanthine*, because it contains one equivalent of oxygen less than xanthine.

GUANINE.

This substance, as its name implies, is obtained from *guano*. This excrement is digested in diluted milk of lime, till the fluid no longer appears brown, but greenish yellow when boiled. It is then filtered, and treated with hydrochloric acid. In a few hours it separates with a little uric acid. It is purified by solution in hydrochloric acid, crystallization, and separation from the acid by ammonia.

It is a yellowish-white crystalline powder, without taste or smell; insoluble in water, alcohol, or ether, soluble in hydrochloric acid and caustic soda. It forms unstable salts with water.

It consists of $C_{10}H_5N_5O_2$, and its atomic weight is 1887.5.

It is found in the excrements of sea-fowl and of spiders. It is probably the *xanthine* which Strahl and Lieberkühn found in human urine.

ALLANTOINE.

When the allantoic fluid of a fœtal calf or the urine of the young animal is evaporated, below the boiling point, to a thin syrup, crystals of allantoine mixed with phosphate and urate of magnesia are formed. The urate of magnesia is washed away from the crystals, and the two remaining substances separated with hot water, which dissolves the allantoine, leaving the magnesian salt. Treatment with animal charcoal and recrystallization purify it.

Fig. 8.

Allantoine.

It occurs in the form of colorless, hard prisms, with a strong vitreous lustre; is tasteless and inodorous; crystallizes from its hot alcoholic solution; is insoluble in ether; dissolves in 160 parts of cold

water and more easily in hot water. It is unalterable in the air; does not redden litmus; and, when heated, chars without fusing. It dissolves, with the aid of warmth, in the caustic alkalies and their carbonates, but crystallizes from them unchanged when they cool. Concentrated caustic alkalies decompose it into oxalic acid and ammonia.

Its formula is $C_8H_5N_4O_5+HO$; its atomic weight, 1862.5.

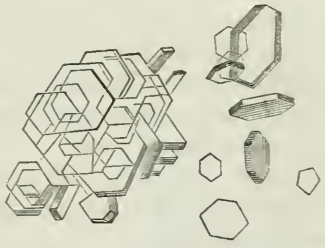
It is found only in the allantoic fluid of the cow's fœtus and in the urine of the newly-born animal. In the urine of sucking calves, it occurs together with uric acid and urea, but without hippuric acid, whence it has been suggested that hippuric acid and allantoine substitute one another in the economy.

CYSTINE.

When certain urinary calculi are dissolved in potash, the addition of acetic acid separates cystine from them. The same substance is obtained by dissolving the calculi in ammonia, and allowing them to crystallize out by spontaneous evaporation.

This body occurs in colorless, transparent, hexagonal plates or prisms. It is tasteless, inodorous, insoluble in water or alcohol. It does not fuse, but burns with a bluish-green flame and a peculiar acid odor.

Fig. 9.



Cystine

Its formula is $C_6H_6NS_2O_4$; its atomic weight, 1336. It combines with a few acids and some salts.

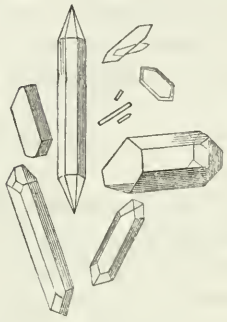
It is a substance of rare occurrence, having been found in but few urinary calculi. Golding Bird and Mandl have found it dissolved in the urine, and it occurs in urinary sediments mixed with urate of soda. It is the only urinary body which contains sulphur, and that metalloid exists in larger proportion in it than in any other organic body, not excepting taurine. The percentage of sulphur in cystine is 26, in taurine 25. Hence,

Lehmann observes, the rational physician should direct his attention to the liver when cystine is found in the urine.

TAURINE.

This substance, formerly called *biliary asparagin*, is obtained from the alcoholic solution of ox-gall by mixing it with hydrochloric acid, boiling it till no more choloidic acid is formed, filtering, evaporating till the chloride of sodium crystallizes out, and then treating the acid mother-liquor with boiling alcohol. Taurine separates in needles as the mixture cools, and is purified by recrystallization from water.

Fig. 10.



Taurine.

It crystallizes in characteristic hexagonal prisms, with four and six-sided sharp extremities, is hard, craunches beneath the teeth; is soluble in 15.5 parts of water, and 573 of spirit of wine.

Its formula is $C_4H_7NS_2O_6$. Its atomic weight has not been determined.

It is recognized by the form of its crystals, by its property of developing sulphurous acid when heated with free access of air, and by its not blackening when boiled with caustic potash, but developing ammonia, and leaving nothing in solution but sulphurous and acetic acids.

Taurine has never been found isolated in the healthy organism, but is supposed to be preformed in the bile, and then conjugated with cholic acid. Of its origin, little is known; of its use, nothing. It has been supposed that it is formed mainly from the sulphur of the albuminous food during its nutritive metamorphosis.

CHAPTER VI.

NITROGENOUS ACIDS.

These have been described by Lehmann as conjugated acids, that is, as acids which are combined with mere basic substances without losing their saturating power. The organic substance, combined with the acid, however, materially alters its properties, while it does not affect its acidity.

Carbazotic or *picric acid* is a yellow, crystalline substance, the result of the action of nitric acid upon many vegetable and animal substances. It is usually obtained by boiling indigo in nitric acid. It has been suggested as a test for potash, but the author's experience with it has been anything but satisfactory.

Its formula is $C_{12}H_2N_3O_{13}+HO$; its atomic weight, 2750; its saturating capacity, 3.636.

HIPPURIC ACID.

Hippuric or *uro-benzoic acid* is a constant constituent of horse's urine. The fresh urine of the horse is evaporated to one-eighth of its volume, and then treated with hydrochloric acid. On cooling, hippuric acid, contaminated with much coloring matter, separates. To purify it, it is boiled with milk of lime, mixed with alum, and the alumina precipitated with bicarbonate of soda. The hippurate of soda is decomposed with hydrochloric acid, the precipitate boiled with animal charcoal, and filtered while hot. The acid now separates colorless, as the solution cools.

Fig. 11.

Hippuric acid.

It crystallizes in minute spangles or larger, obliquely-striated, four-sided prisms. Its elementary form

is a vertical rhombic prism. It is bitter, inodorous, soluble in 400 parts of cold water, very freely in hot water and in alcohol, but insoluble in ether. Gently heated, it fuses; with a stronger heat, a crystalline sublimate of benzoic acid and benzoate of ammonia is obtained, while a few oily drops appear, which emit an odor of cumarin, the oil of Tonka bean. A higher heat reduces the acid to a porous coal, with the development of a very strong odor of hydrocyanic acid. In fermenting or putrefying fluids, it is decomposed into benzoic acid and unknown products.

Its formula is $C_{18}H_8NO_5+HO$, its atomic weight 2125, and its saturating capacity 4.706. Its constitution has been variously expounded by different chemists, and nothing definite has yet been determined. It has been supposed to be glycine conjugated with benzoic acid.

Benzoic acid is the only one with which it is likely to be confounded, but it may be distinguished from it by its method of crystallization. Hippuric acid crystallizes from hot solutions in prisms, benzoic acid in scales.

Liebig has shown that this acid exists in small quantity in healthy human urine. In various forms of disease, it is also found. In febrile urine, it is often present. It occurs also in diabetes, and has been found in the urine of drunkards and of patients suffering with chorea. It is rapidly formed after the ingestion of benzoic acid. Its origin is unknown, but it probably comes from the *debris* of the albuminous tissues.

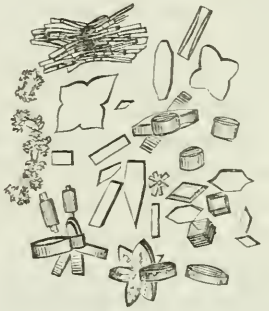
URIC ACID.

The best process for obtaining uric acid is that devised by Bensch. It consists in boiling the excrements of serpents, or of birds, or uric acid calculi in a solution of one part of hydrated potash in twenty parts of water till no more ammoniacal fumes are evolved. Carbonic acid is passed through the solution till the alkaline reaction nearly disappears. The precipitated urate of potash is washed in cold water till it begins to dissolve; it is then dissolved in a solution of potash, warmed, and treated with hydrochloric acid, when pure uric acid precipitates.

It occurs either in a glittering white powder or in very minute scales, which, under the microscope, are seen to be made up of irregular plates. It is soluble in 1800 parts of hot and 14,000 parts of cold water, insoluble in alcohol and ether, and does not redden litmus. It dissolves readily in carbonates and other alkaline salts. It is disengaged from its combinations by acetic and other acids, and forms a gelatinous mass, changing into small glistening plates.

It is one of the weakest of the acids. It does not disengage carbonic acid from carbonate of potash, but gives rise to the formation of urate and bicarbonate of potash if added in sufficient quantity. In a concentrated solution, the urate of potash remains undissolved.

Fig. 12.



Uric acid.

By dry distillation it is converted into urea, cyanic acid, cyamelide, hydrocyanic acid, and carbonate of ammonia, and leaves a brownish-black coal, rich in nitrogen. Fused with hydrated potash, carbonate and cyanate of potash with cyanide of potassium are formed. In nitric acid it dissolves, giving off equal volumes of nitrogen and carbonic acid. On evaporating this solution to dryness, a red amorphous residue (murexide) remains, which, exposed to the vapor of ammonia, assumes a very beautiful purple tint; and is rendered violet-colored by treatment with caustic potash.

Its formula is $C_5HN_2O_2+HO$, its atomic weight 937.5, and its saturating capacity 10.656. Several theories have been advanced to explain its constitution, but all have fallen to the ground.

It forms soluble and neutral salts with the fixed alkalies; with ammonia and other bases, it forms only acid and insoluble compounds.

The products of the metamorphosis of uric acid are very numerous, and have been carefully studied, but as yet they possess little or no physiological interest. It would take up too much

space to recount all these bodies, and the reader is therefore referred to Golding Bird's *Urinary Deposits*, Simon's *Animal Chemistry*, and the excellent work of Lehmann, already so often quoted and so frequently referred to.

Uric acid is easily recognized by the *murexide test*, that is, by evaporating to dryness, and adding caustic potash, when the red amorphous residue will assume a fine violet color. The microscope also readily detects this substance, since its crystalline forms, though various, are so very remarkable.

The quantitative estimation of it in the urine is easily made by dissolving out the earths with hydrochloric acid from the residue left after extracting evaporated urine with alcohol. Uric acid and mucus remain. The first is taken up by dilute solution of potash, and the urate of potash decomposed by means of acetic acid. In determining its presence in albuminous fluids, it is necessary to evaporate to dryness, extract with alcohol and water, and seek for the acid in the watery solution.

Uric acid is always found in the urine of healthy men, in the proportion of about one part in every thousand of urine. The nature of the food exerts very little influence over the proportion of this ingredient. It is a little increased by an animal and slightly diminished by a vegetable diet.

It has been generally stated that the increased activity of the skin in summer was unfavorable to the discharge of uric acid by the kidneys. Lehmann, however, declares that the only result he was able to arrive at, after a number of experiments, was, that the amount of water in the urine was increased in winter and diminished in summer, but that the solid constituents, especially the acid under consideration, was neither increased nor diminished.

In disturbed or imperfect digestion, the amount of this substance is usually very much increased. In fever, also, there is more uric acid formed than in health. The deposit which almost always clouds the acid urine of febrile patients consists of urate of soda. Its occurrence in acid urine may be easily explained by its property of decomposing the alkaline salts, and forming with them acid urates, while it allows a portion of the neutral salt to combine with the excess of acid expelled in order to form

the urate. In this manner, acid salts must be formed on both sides.

Uric acid, in the form of urate of soda, is deposited in the joints in great quantity during gout, though it is denied by several chemists, Garrod and Lehmann among them, that any increase of the secretion of this substance takes place in that disease.

This acid also exists in the blood, both in health and in disease.

Uric acid is undoubtedly an excrementitious substance, and is in all probability one of the intermediate stages between decomposed tissue and urea, the latter substance resulting from its oxidation. The experiments of Wöhler and Frerichs on uric acid show that when it is injected into the veins or introduced into the stomach, the urea and the oxalate of lime in the urine are increased, a fact which is regarded as conclusive proof of the theory just mentioned. Anything, therefore, diminishing or retarding the oxidation of this acid, must give rise to an increase of the unchanged substance in the urine.

INOSIC ACID.

Liebig obtained this acid from the juice of flesh, after creatine had crystallized out, by treating it with alcohol till crystals formed, redissolving these in hot water, precipitating by chloride of barium, and decomposing with sulphuric acid. It is a syrupy fluid, soluble in water, insoluble in alcohol and ether, reddening litmus strongly, and having an agreeable taste of the juice of meat.

Liebig's formula, calculated from the baryta salt, is $C_{10}H_6N_2O_{10}+HO$. Its atomic weight is 2175, its saturating capacity, 4.597.

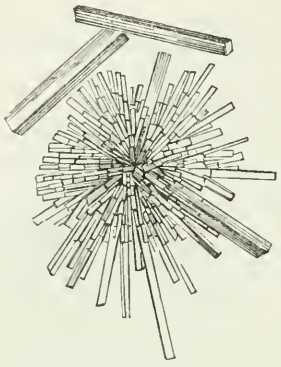
GLYCOCHOLIC ACID.

This acid is obtained by precipitating fresh bile with sugar of lead, extracting the precipitate with boiling alcohol of 85 per cent., passing sulphuretted hydrogen through the solution, fil-

tering, adding water, and allowing the mixture to stand till the acid is deposited in crystals.

It forms very delicate needles, of a bitterish sweet taste, soluble in 120.5 parts of hot and 303 of cold water, easily soluble in alcohol, but slightly in ether. It dissolves readily in alkalies, and is precipitated from them, as a resinous mass, by the addition of acids. Prolonged boiling with caustic potash or baryta water resolves it into cholic acid and glycine.

Fig. 13.



Glycocholic acid.

Its formula is $C_{52}H_{42}NO_{11}+HO$. The atomic weight of the hypothetical anhydrous acid is 5700, its saturating capacity, 1.754.

This acid is found in the bile of all animals yet examined for it with the exception of the pig. It is manifestly cholic acid conjugated with glycine, but of its origin or use nothing is yet positively known.

TAUROCHOLIC ACID.

This is an acid conjugated with taurine, as the one last described is with glycine. It is obtained from the bile by precipitating first with acetate of lead, filtering, and precipitating the filtrate with basic acetate of lead, to which a little ammonia may be added. The precipitate is decomposed with carbonate of soda, filtered, and extracted with alcohol. Ether, added to the alcoholic solution, precipitates taurocholate of soda, as a resinous, semifluid, yellow mass. This is to be dissolved in water, the solution precipitated with acetate of silver, the filtered fluid thrown down with acetate of lead, the precipitate suspended in water and decomposed with sulphuretted hydrogen. Sulphuret of lead is filtered off, and the clear solution, evaporated in alcohol, gives tolerably pure taurocholic acid.

This substance was formerly called *bilin*, and has also received

the name of *choleic acid*. It dissolves fat, fatty acids, and cholesterin in large quantities; boiled with alkalies, it is decomposed into taurin and cholic acid.

Its formula is $C_{52}H_{45}NS_2O_{14}$.

It is found in the bile of most animals, and probably exists in that of man. Its origin and chemical action upon the food are alike unknown.

CHAPTER VII.

NON-NITROGENOUS ACIDS.

The acids of the human body which do not contain nitrogen are very numerous. For the sake of perspicuity, they have been divided into several groups.

THE BUTYRIC ACID GROUP.

The general formula of this group is $C_nH_{n-1}O_3+HO$.

The acids composing it form salts which are usually soluble, and easy of crystallization. They were formerly called *volatile fatty acids*, but that name is now abandoned by most chemists, because it was based upon a misconception of their true origin.

From these acids, may be obtained a series of liquid volatile fluids, called *aldehydes*, which, on exposure to the air, absorb oxygen, and are converted into their corresponding acids. Their general formula is $C_nH_{n-1}O+HO$.

Isomeric with them is another series of compounds obtained from the dry distillation of the baryta salts of these acids. They are oily, volatile, pungent fluids, soluble in alcohol and ether, but not in water, volatilizing without decomposition, and devoid both of acid and basic properties. They are distinguished by the termination in *al*. Their isomerism with the aldehydes may be seen by the following example. *Butyric aldehyde*, $C_8H_7O+HO=(CH)_8O_2$, *butyral*.

There is still another series of derivatives, known by the termination *one*, obtained from the strong basic salts of these acids by heating them. The acid loses the elements of carbonic acid, which remains combined with the base, and a colorless, volatile, pungent, highly inflammable oil distils over. Thus, *butyrate of lime*, when heated, is resolved into carbonate of lime and *butyrone*, *e. g.* $CaO,C_8H_7O_3 = CaO,CO_2 + C_7H_7O$.

These acids are excellent exemplifications of the substitution theory, the hydrogen in them being replaceable by other elements, especially chlorine, iodine, and bromine. Thus, when chlorine and acetic acid come together, hydrochloric and chloracetic acids are formed, for $C_4H_3O_3.HO + 6Cl = 3HCl + C_4Cl_3O_3.HO$.

Amides are also formed from the ammonia salts by the loss of an atom of water. Acetate of ammonia is resolved into acetamide and water; $H_3N.C_4H_3O_3 = H_2N.C_4H_3O_2 + HO$. The substitution theory is inapplicable to these changes. The amides are solid, crystallizable, colorless, indifferent, volatile substances. Treated with nitrous acid, they are converted into the acids with the development of ammonia.

When the amides of these acids are treated with anhydrous phosphoric acid, they lose water, and nitriles remain, which contain the radicle of the acid and one equivalent of nitrogen in place of three of oxygen. Thus *butyramide* and phosphoric acid form hydrated phosphoric acid and *butyronitrile;* $C_8H_9NO_2 + PO_5 = PO_5 2HO + C_8H_7N$.

The *nitriles* are oily, volatile, odorous fluids, less soluble in water than in alcohol or ether; can be distilled without decomposition, and are neither acid nor basic. Kolbe regards these acids as carbo-hydrogens conjugated with oxalic acid.

OXALIC ACID.

This acid is a product of the oxidation of most animal and vegetable substances, and is usually obtained by decomposing sugar or starch with slightly dilute nitric acid, and crystallizing.

It crystallizes with three atoms of water in oblique rhombic prisms. It has a sharp acid taste, but no odor. It effloresces

on exposure to the air, losing two atoms of water, and when carefully heated, may be sublimed without decomposition, but at from 300° to 340° it is decomposed into formic and carbonic acids, carbonic oxide and water. Boiled with salts of gold, carbonic acid escapes, and finely divided metallic gold falls.

Its formula is C_2O_3+HO; its atomic weight 450; its saturating capacity, 22.222. It has been variously regarded as the oxide of a hypothetical radical *oxalyl*, C_2O_2, a dinoxide of carbonic oxide, or a hydrogen acid C_2O_3H.

Oxalate of lime is an important salt in pathological chemistry, being a very frequent urinary deposit. It is amorphous to the naked eye, but under the microscope is seen to be crystallized in square octahedra, resembling chloride of sodium, from which they are distinguished by their insolubility in water.

Oxalic acid is recognized by its behavior with salts of gold, which it reduces to the metallic state, and by its not charring when heated, or mixed with sulphuric acid.

Oxalic acid was long regarded as a purely pathological product, but it has been shown that it is a constituent of normal human urine. Schmidt supposed that it was formed from the mucus of the bladder, but Lehmann has obtained it from urine thoroughly deprived of its mucus. It is increased in a great variety of diseases, especially those accompanied by pulmonary obstruction, or by weakness of the respiratory act. It is also augmented by the use of sparkling wines and of beer highly charged with carbonic acid, as well as of vegetable food containing oxalates.

Thus, it may be transmitted directly from the food to the urine, but its usual mode of production is, most probably, an incomplete oxidation of uric acid and other constituents of the blood, that process being arrested before the formation of carbonic acid could be accomplished. It is easy to explain, on this view, the increase of this substance after the ingestion of carbonic acid, and during the various disturbances, functional or structural, of the respiratory organs.

FORMIC ACID.

This acid does not exist, so far as yet known, in the human body. It was originally obtained, as its name implies, from ants, by distillation. Even in them, however, it appears to have existed in the food, and not to be formed in the body. It is a common result of the oxidation of various animal and vegetable substances. It is usually obtained by distilling a mixture of a little dilute sulphuric acid with three parts of sugar, and one of bichromate of potash.

It forms two distinct hydrates, reduces the oxides of silver and mercury, and is decomposed into water and carbonic oxide by the action of sulphuric acid.

Its composition is C_2HO_3HO; its atomic weight 462.5; its saturating capacity, 21.62. It has been regarded as an oxalic acid conjugated with hydrogen, and as an oxide of an hypothetical radical *formyl*, C_2H, which is believed to occur in other combinations, as for instance in *chloroform* (terchloride of formyl), C_2H,Cl_3.

ACETIC ACID.

This is a well known result of the oxidation of alcohol. To it our common vinegar owes its acidity. A variety of methods have been used to obtain it. It is most conveniently procured, for ordinary chemical purposes, by distilling a mixture of dilute sulphuric acid, sulphate of soda, and neutral acetate of lead.

In its most concentrated state it is a crystalline mass below 60°; above this temperature it is fluid, has a specific gravity of 1.080, and boils at 243.1°.

Its formula is $C_4H_3O_3$, HO; its atomic weight (anhydrous), 637.5; its saturating capacity, 15.686.

Nitrate of suboxide of mercury precipitates from it, after some time, minute crystalline specks, falling in glistening, fatty-looking scales. It strikes a red tint with persalts of iron, a property which it possesses in common with meconic and hydrosulphocyanic acids. From the former it is distinguished by its

property of dissolving lime; from the latter by the fact that, sulphocyanide of iron is precipitated *blue* by *ferridcyanide of potassium*, after being warmed awhile with it.

It is uncertain whether this acid is found ready formed in the healthy human body. It is one of the products of the digestion of alcohol, and is often found in the gastric juice of dyspeptics. It has been discovered in vomited matters, when only vegetables and meat, and no vinegar, had been eaten.

METACETONIC ACID.

This acid, which is closely allied in some respects to nitric acid, has been supposed, from analogy, to exist in the human body, though it has never been detected in it. It is formed during the spontaneous decomposition of many vegetable substances, in the oxidation of albuminous bodies, and the fermentation of glycerin with yeast. It is ordinarily prepared by treating one part of sugar with three of hydrated potash, and separating the other acids, oxalic, formic, and acetic from it.

It has also been called *butyro-acetic* and *propionic acid*. It forms, when concentrated, a colorless, oily fluid, solidifying at a low temperature, boiling at about 285°, and having a peculiar taste, resembling that of sauer-kraut.

Its composition is $C_6H_5O_3.HO$; its atomic weight (anhydrous) 815.5; its saturating capacity, 12.31. Kolbe regards it as an ethyloxalic acid.

BUTYRIC ACID.

This acid is present in rancid butter, and was obtained by Chevreul during the saponification of butter. It is usually prepared by mixing sugar, sour milk, and cheese together, and exposing them for five or six weeks, or as long as gas escapes, to a summer temperature, *i. e.* from 85° to 95°. The fluid is filtered, decomposed with carbonate of soda, filtered again, concentrated, decomposed with sulphuric acid, and distilled. The butyric acid, which comes over, is freed from water and acetic acid by fused chloride of calcium.

It is an oily fluid, and can only be solidified by the intense

cold (—183°) induced by mixing solid carbonic acid with ether, when it crystallizes in plates. It evaporates at the ordinary temperature, but does not boil below 315°. When inflamed, it burns like an ethereal oil.

Its formula is $C_8H_7O_3.HO$; its atomic weight (anhydrous), 987.5; its saturating capacity, 10.126.

It has been found in the *milk*, the *feces*, the *urine* of pregnant women, and women who do not suckle their children, the *sweat*, especially of the genitals and the lower extremities. The nauseous, acrid, or rancid substances occasionally vomited from the stomach, undoubtedly owe this odor to butyric acid. When met with in the *primæ viæ*, it is probably formed from the non-nitrogenous constituents of the food. When it occurs in the sweat, blood, and urine, it is most likely a result of regressive metamorphosis, owing its origin to the disintegration of the tissues, or the gradual oxidation of the fats.

VALERIANIC ACID.

This acid, as well as others of this group whose amount of carbon is divisible by two and not by four, has never been found in the human body. It is, however, interesting, as one of the results of decomposition of animal and vegetable matter.

It has a characteristic odor, an acrid, burning taste, and produces a white spot on the tongue. It remains fluid at 5°, boils at 349°, and dissolves in 26 parts of water.

Its formula is $C_{10}H_9O_3.HO$; its atomic weight (anhydrous), 1162.5; and its saturating capacity, 8.602.

CAPROIC ACID.

This is a somewhat thin liquid with an odor resembling that of sweat. It is obtained by saponifying butter, or decomposing oleic acid with fuming nitric acid, or by acting on albuminous bodies with peroxide of manganese or chromic acid.

Its formula is $C_{12}H_{11}O_3.HO$; its atomic weight (anhydrous), 1337.5; its saturating capacity, 7.476. Kolbe regards it as amyloxalic acid.

From its odor, it has been supposed to exist in sweat. Lehmann says, it has not been sought for in the contents of the stomach or in the urine. It happened to the author, on one occasion, while making the analysis of the contents of a negro's stomach for arsenic, to use Reinsch's test in a portion of the fluid not thoroughly freed from organic matter. The brilliant surface of the copper became, after protracted boiling, covered with an olive-brown, slightly lustrous coating, which dissolved in caustic ammonia; and, when heated, burned with a green flame, emitting the characteristic odor of negro's sweat. No farther examination of it was made, and the fact is here stated for what it is worth.

ŒNANTHYLIC ACID.

This is a colorless, oily, inflammable liquid, of a faint aromatic odor and taste, produced during the decomposition of fats. It is usually obtained by the action of nitric acid on castor-oil. Its formula is $C_{14}H_{13}O_3.HO$.

CAPRYLIC ACID.

This is another of the acids formed during the saponification of butter, and by the reaction of nitric and oleic acids. Its formula is $C_{16}H_{15}O_3.HO$.

Pelargonic acid ($C_{18}H_{17}O_3$).HO, found in several plants and produced by acting on oleic or choloidic acid, by nitric acid; *capric acid* ($C_{20}H_{19}O_3.HO$), obtained from oil of rue, and *cetylic acid* ($C_{32}H_{31}O_3.HO$), procured from spermaceti, require no special notice here.

SUCCINIC ACID GROUP.

The general formula of these acids is $C_nH_{n-2}O_3.HO$. They are products of the decomposition of animal matters, especially of the fats. They are all formed by the action of nitric on oleic acid. They are crystallizable, volatile at a high heat with

a suffocating odor, and yield oxalic acid when fused with hydrate of potash. None of them are preformed in the animal body, and their only physiological interest consists in their being products of decomposition.

Succinic acid ($C_4H_2O_3.HO$), as its name implies, was originally obtained by the dry distillation of amber. It occurs, however, as a product of the decomposition of fat and of various kinds of fermentation. When perfectly anhydrous, it occurs in very delicate needles, with one atom of water; it crystallizes in oblique rectangular prisms.

Fig. 14.

Sebacic acid.

Sebacic acid ($C_{10}H_8O_3.HO$) is obtained during the dry distillation of oleic acid. It forms white, nacreous, acicular crystals grouped in loose heaps. It fuses at 260° into a colorless liquid, which, on cooling, solidifies into a crystalline mass. It is slightly soluble in cold water, freely in hot water, alcohol, and ether. It reddens litmus, has a pungent taste, and is converted, by nitric acid, into paratartaric acid. Its formula is $C_{10}H_8O_3.HO$.

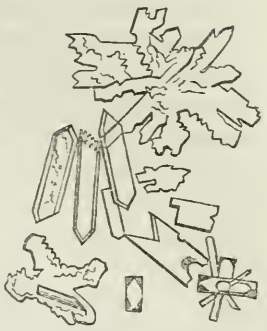
BENZOIC ACID GROUP.

The general formula of this group is $C_nH_{n-9}O_3.HO$. With the exception of benzoic acid, they possess but little interest for the physiologist. They are solid, crystallize readily in needles or scales, are fusible, slightly soluble in cold, readily in hot water. They have aldehydes, amides, and nitriles like the acids of the former group.

Benzoic acid ($C_{14}H_5O_3.HO$) is the only one to which we shall call attention. It is a pharmaceutical substance, and is commonly obtained by the sublimation of gum benzoin. When thus procured, it occurs in colorless, delicate needles; obtained in the moist way, it crystallizes in scales, minute prisms, or six-sided

needles. It fuses at about 250°, boils at 462°, being converted into a thick, irritating vapor, and it is not decomposed by sulphuric or nitric acid. The products of its metamorphosis are oil of bitter almonds, benzamide, and several other substances, which have recently been very carefully studied, but which we have not room here to consider.

Fig. 15.



Benzoic acid.

The influence of benzoic acid, in increasing the quantity of hippuric acid in the urine has already been noticed. Liebig thought, at one time, that it was discharged originally in the urine of ill-fed and hard-worked horses; changing his former view, that it was a product of decomposition out of the body. The subject has been examined by Lehmann, and he has come to the conclusion that Liebig's earlier opinion is the correct explanation of its formation.

LACTIC ACID GROUP.

The formula of this group, which contains but few individual acids, is $C_nH_{n-1}O_5.HO$; when deprived as much as possible of water, they are oily, non-crystallizable fluids.

Lactic acid ($C_6H_5O_5.HO$), in its most concentrated state, is a colorless, inodorous, thick, syrupy fluid, of specific gravity 1.215; soluble in water, alcohol, and ether, attracting water from the air, decomposing by heat, and displacing many oxides from their salts. The relations of the acid differ, as it is obtained from muscular juice; or from sugar, especially in the amount of water of crystallization and the degree of solubility of the salts.

It is formed during the fermentation of fluids containing sugar or starch. Bensch's process is, to mix 6 parts of cane-sugar, $\frac{1}{16}$ of tartaric acid, 8 of sour milk, $\frac{1}{2}$ of old cheese, 3 of levigated chalk, and 26 of water, and to expose them for eight or ten days to a temperature of 90°. A semi-solid magma of lactate

of lime is formed, which is boiled with 20 parts of water and $\frac{1}{16}$ of caustic lime, filtered while boiling, slightly evaporated, and set aside a few days to crystallize. The salt is dried, pressed, treated with $\frac{7}{32}$ of sulphuric acid, filtered, and the clear fluid saturated with $\frac{3}{10}$ of carbonate of zinc and crystallized. The zinc and salt is decomposed with sulphuretted hydrogen, and the fluid concentrated first by heat, afterwards *in vacuo*, and the hydrated acid obtained by solution in ether.

Liebig procures it from the juice of flesh after the separation of creatine.

It is one of the most difficult to recognize of all the acids found in the animal body. It requires a thorough knowledge of its various reactions, and especially of the microscopic characters of its salts, to arrive at anything like a correct opinion.

The question so long discussed, whether free lactic acid forms a part of healthy gastric juice may now be considered as decided in the affirmative. This acid is a constant constituent of the juice of flesh, or the muscular fluid. It is also found in the secretion bathing mucous surfaces and in the sweat. In diabetes mellitus, it occurs in the saliva, and has been found in the blood in several forms of disease. It has not yet been detected in healthy blood, though it probably exists there, the failure to determine its presence being due to the imperfection of the present appliances of analytical chemistry, as well as to the rapidity with which it is converted into carbonic acid. Lehmann found carbonate of soda making its appearance in the urine within five minutes after the injection of lactate of soda into the jugular vein of a dog. It is also present in the urine, in persons who have fed largely on food containing lactates, or whose respiratory functions have been impaired. It is always found in urine containing any considerable quantity of oxalate of lime. It has been observed in the fluid yielded by the long bones in a case of osteomalacia.

The lactic acid, formed in the intestinal canal, probably results from the decomposition of the vegetable food, while that in the muscles would appear to arise from the metamorphosis of various animal substances, among others, the glycerine basis of the fats.

In the stomach, it is supposed to play an important part in the digestion of the food; while in the *blood*, it seems to form a part of the respiratory food. In the *muscles*, Liebig supposes that, by reacting on the alkaline blood of the capillaries, it keeps up an electric tension which influences the function of the muscles. In the *sweat* and *urine*, it is a product of excretion.

SOLID FATTY ACIDS.

Lehmann gives as the general formula for this group $C_mH_{m-1}O_3.HO$, which shows at a glance the close relation between this and the first-described group of non-nitrogenous acids. They differ, however, in having a higher atomic weight, and in several other particulars. At common temperatures, they are solid, white, crystalline, tasteless, inodorous, soluble in ether and in boiling alcohol, insoluble in water, inflammable, and fusible below 212°. They leave on paper a fatty spot which does not disappear, expel carbonic acid from its salts by the aid of heat, and have a strong tendency to form insoluble salts with metallic bases.

Very few of them have been found in the animal body.

MARGARIC ACID.

This acid crystallizes in pearly needles (whence its name), which under the microscope appear interlaced like tufts of grass, and arranged in plates or grouped in star-like forms. It can only be partially distilled unchanged, carbonic acid and *margarone* being formed. By prolonged contact with nitric acid, it is decomposed into succinic, suberic, and carbonic acids and water.

Its formula is $C_{34}H_{33}O_3.HO$, its atomic weight 3262.5.

It is obtained by saponifying human fat or olive oil with potash, and decomposing with sulphuric acid. The fatty precipitate is well washed with water, thoroughly dried, and pressed strongly between bibulous paper to get rid, as much as possible, of oleic acid. By repeated crystallizations from hot alcohol, the stearic acid, which falls first, is separated; and the oleic acid is got rid of by precipitating with acetate of lead, and dissolving

out the oleate of lead with boiling ether. The margarate of lead is decomposed by an alkaline carbonate, and the resulting alkaline margarate by a stronger acid.

Margaric acid is a common constituent of fats. It is found free in the feces after vegetable food or purgative medicine has been taken, and in acid pus from cold abscesses. The finest possible crystals may be obtained by carefully fermenting pus.

STEARIC ACID.

This acid, which is usually prepared from mutton fat as already described, crystallizes in white glistening needles or leaflets, appearing under the microscope as elongated lozenge-shaped plates, with the obtuse angles rounded off. Digestion with nitric or chromic acid converts it into margaric acid.

Its formula is $C_{68}H_{66}O_5.2HO$, its atomic weight, 6425.

It occurs in most animal fats, and must be formed in the body, since it is not found in vegetable fats. It is probably formed from margaric acid, since it is equivalent to two atoms of that acid *less* one of oxygen.

OILY FATTY ACIDS.

This group contains but few acids; its general formula is $C_mH_{m-3}O_3.HO$.

OLEIC ACID.

Oleic or *elaic acid* is at ordinary temperatures an oily, limpid, colorless, tasteless, inodorous fluid, solidifying at 39° to a white crystalline mass, which contracts and forces out the still oily portion. An alcoholic solution, exposed to intense cold, crystallizes in long needles. It is decomposed by heat, giving off carbonic acid and carbo-hydrogens, and forming also capric, caprylic, and sebacic acids, and carbon.

Its formula is $C_{36}H_{33}O_3.HO$, its atomic weight (anhydrous) 3412.5.

Eläidic acid is isomeric with it, but crystallizes from alcohol in large plates instead of needles.

After having separated the *oleate of lead* as already described, this salt is decomposed with carbonate of soda and the soda-salt with sulphuric acid. The brown oleic acid thus obtained is to be treated with excess of ammonia, precipitated with chloride of barium and the baryta-salt; after being purified by repeated crystallizations from boiling alcohol, is to be decomposed with tartaric acid, and thoroughly washed with water.

It exists in greater quantity in vegetable than animal fats, and is supposed to serve as a basis for the formation of the solid fatty acids.

Doeglic acid, having only been found in the oil of a certain variety of whale (*balœna rostrata*), need not occupy our attention.

RESINOUS ACIDS.

LITHOFELLIC ACID.

This acid has only been obtained from *bezoars*, the intestinal concretions of certain goats. It crystallizes in small six-sided prisms, volatilizes in white vapors with an aromatic odor, fuses at 400°, and solidifies in a crystalline form.

Its formula is $C_{40}H_{36}O_7.HO$.

CHOLIC ACID.

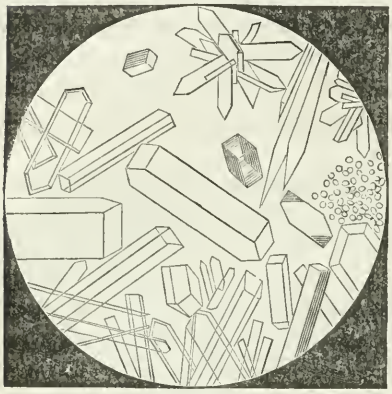
Cholic acid is obtained by precipitating the alcoholic solution of bile with ether; digesting the resinous mass that falls with a dilute solution of potash for twenty-four or thirty-six hours, till the potash salt begins to crystallize. This must then be dissolved in water, and decomposed with hydrochloric acid. A few drops of ether convert the resinous mass into a crystalline, solid, pulverizable substance. It is to be reduced to powder, washed with water, crystallized in alcohol, and treated with ether to remove coloring matters.

It crystallizes in tetrahedra, octahedra, or rhombic prisms; has a bitter taste and a sweetish after-taste; is slightly soluble in water, easily in alcohol, and with more difficulty in ether; burns with a clear flame, and is decomposed by hydrochloric acid into *choloidic acid* and *dyslysin*.

Its formula is $C_{48}H_{39}O_9.HO$, according to Strecker; $C_{50}H_{36}O_6 + 5HO$, according to Mulder.

It, together with bile and biliary derivations which always contain it, is recognized by Pettenkofer's test. The alcoholic extract is dissolved in a little water, a drop of syrup containing one part of sugar to four of water let fall into it, and pure English sulphuric acid, free from sulphurous acid, dropped cautiously into the mixture. It first becomes turbid, then, as the acid is gradually added, clears up again, and becomes first yellowish, then cherry-red, then a deep carmine, then purple, and finally violet. To use this test properly, excess of sugar must be avoided, and the temperature should approach but never exceed 122°. The fluid must also be allowed to stand awhile. This test, however, cannot be inverted, and used for the detection of sugar, for the same change takes place with acetic acid.

Fig. 16.



Cholic acid.

Cholic acid is easily detected by the above test in the whole small intestine, and a diagnosis of the seat of artificial anus has been made by its aid. Pettenkofer failed to detect it in the healthy feces, though he found it in the discharge of diarrhœa. Lehmann, however, obtained the reaction by dissolving the alcoholic extract of feces in ether, separating the fats with water, and testing the concentrated aqueous solution of the ethereal extract.

This substance has so many points of resemblance with the fatty acids that it is thought probable that it, with other biliary substances, is formed from the fats. It has been supposed to be oleic acid conjugated with a radical, $C_{12}H_6O_6$.

CHAPTER VIII.

NON-NITROGENOUS BASES AND SALTS—HALOIDS.

This is the title given by Berzelius to a class of organic compounds which differ from those we have already been considering. The term is derived from the Greek word for salt, and implies that these bodies are analogous to common salt in chemical constitution. A word or two in reference to certain peculiarities of combination in the inorganic world will constitute a suitable preface to our account of these organic salts and their bases.

A salt is usually called a compound of a base and an acid, and it was at one time thought that all of them were made up by the union of oxygen and a metal to form a base, the union of oxygen with a metalloid to constitute an acid, and the combination of these two bodies, the base and the acid, to produce the salt. On a more minute examination, however, it was found that this was by no means the invariable constitution of salts. It is true, undoubtedly, of a very large number of this class of compounds, of which the sulphate of potash may be cited as an example. In it, the component parts are the base, potash, the oxide of a metal, potassium, and the acid, sulphuric, the oxide of a metalloid, sulphur. The formula, therefore, of the perfectly anhydrous salt would be KO,SO_3.

According to this view, therefore, common salt was called a muriate of soda, and the soda was thought to be combined with the muriatic acid, just as the potash is with the sulphuric acid in the last-mentioned case. It was discovered, however, that the old muriatic acid is a hydracid, that is to say, that it contains no oxygen, but is formed by the union of chlorine and hydrogen, and that in combining with soda, it loses its hydrogen, and the base parts with its oxygen, so that there is a direct union of the metalloid with the metal, the former parting with its acidifying, the latter with its basic principle. This salt, therefore, is constituted according to the formula Na,Cl, a totally dif-

ferent method of combination from what obtains among the oxysalts.

Farther investigations have shown that there may be sulpho-bases, and sulphacids, and sulpho-salts; that is, that sulphur may play the part of oxygen, forming a base on one hand and an acid on the other, and that these two substances may afterwards unite to form a substance crystallizable, decomposable, and, in every respect, entitled to the appellation, salt. An example of this is found in the yellow crystals obtained by evaporating a solution of arseniate of potash through which sulphuretted hydrogen has been passed. In them, the potassium is proved to exist as a sulphuret or a sulpho-base, and the acid also as a sulphuret or sulphacid. There are other substances which exhibit the same properties in this respect as sulphur. From these peculiarities two classes of salts have been established, the *amphid* salts, which, like sulphate and sulpharseniate of potash, consist of an acid and a base, each of which is composed of two elements; and the *haloid* salts, in which there is direct union between a metal and a halogen (for so iodine, chlorine, bromine, and the compound substances, such as cyanogen, which form salts of this type, have been called).

Ammonia, being a compound body, furnishes an excellent example of these two modes of combination. This substance when free as a gas is represented by the formula NH_3. In this form, it unites with the dry oxacids to form substances called by Rose ammones, which are totally different from the salts of the same acids, the latter being never formed without the intervention of water. The chlorine salt of ammonia was formerly supposed to have the constitution NH_3,HCl. The analogy of other chlorides, however, compelled chemists to assume a new radical (NH_4) having the nature of a metal; a view which is strengthened by the formation of the *ammoniacal amalgam*. Hence, the chloride is represented as NH_4Cl. The oxysalts, which were formerly regarded as combinations of the acids with ammonia, united with one atom of water, are now considered to be formed by the union of the acid with an oxide of the base NH_4. Thus, sulphate of ammonia, instead of being NH_3,SO,HO, is now expressed by the formula NH_4O,SO_3.

Now, if these metamorphoses of ammonia be compared with the constitution of the alkaloids, and of the bases of the fats, it will be found that the theory which supposes the basicity of the nitrogenous alkaloids to be explicable on the hypothesis of a conjugated ammonia, will not hold good in the case of the latter class of bodies. They are basic also, and contain no nitrogen. We have seen, however, that an acid may combine with the oxide of a compound of nitrogen and hydrogen, and we may suppose that the same union may take place with the oxide of a hydrocarbon. These oxides, however, are just as unknown in their isolated state, as is the oxide of ammonia, and many of them, ether for example, were for a long time not suspected of being basic. They form both acid and neutral salts, the former of which have been classified among the conjugated acids, and the latter not regarded as salts at all.

OXIDE OF LIPYL.

When any of the fats are boiled in water with the alkalies, the alkaline earths, or the oxides of the metals, compounds are formed between the fatty acids and the inorganic bases, while a sweet, uncrystallizable substance remains, which has been called glycerine. On weighing the products, an increase of weight is found to have taken place, and this can only come from the water which is essential to the operation. It was supposed that these facts could be explained by assuming that the fatty acid was combined with glycerine, from which it was separated by the stronger affinity of the inorganic bases. On examination, however, it was discovered that the body combined with the fatty acid was composed according to the formula C_3H_2O, while the investigation of glycero-sulphuric acid showed that glycerine must be expressed by $C_6H_7O_5$. It is, therefore, probable that the true base of the fats, not yet isolated, and to which Berzelius has given the name of *Oxide of Lipyl* (*lipyl* being the hypothetical radical C_3H_2), has, during the process of decomposition, assimilated water, and been converted into a new body, *glycerine*.

GLYCERINE.

When the fluid which remains after the manufacture of lead plaster is examined, it is found to contain an organic substance, and a little oxide of lead. If the latter be thrown down by passing a stream of sulphuretted hydrogen through the solution, a black sulphuret of lead subsides, and the watery solution of glycerine remains. This is to be evaporated first in the water-bath, and then *in vacuo*.

Thus obtained, it is a pale-yellowish fluid, sweet to the taste, attracting water from the atmosphere, soluble in water and alcohol, but not in ether, inflammable, and indifferent towards the vegetable colors. It dissolves the alkalies and metallic oxides, and, when oxidated, gives rise to a variety of acids, which differ with the degree of oxidation. By ordinary fermentation it is converted into metacetonic acid.

Pelouze's formula for it is $C_6H_7O_5.HO$. It is not a hydrate of the oxide of lipyl, but a distinct body, which unites with acids to form acid salts, that have been usually regarded and named as compound acids. The products of its metamorphosis are *acrolein*, *acrylic acid*, and *disacrone*.

The best test for glycerine is to heat it rapidly alone, or with a little anhydrous phosphoric acid, when, if it be sufficiently diluted, the peculiar and disagreeable odor, resembling that of the wick of a half-extinguished oil-lamp, is developed.

Glycerine has been found in the yolk of the egg, and in the fats of the brain, in the form of the phosphate of glycerin-ammonia. It has been supposed that, during the oxidation of the fats in the organism, glycerine is formed, and subsequently converted into metacetonic acid.

SALTS OF OXIDE OF LIPYL OR FATS.

These substances are usually soft and greasy at common temperatures, though some of them are firm and waxy, and a few liquid. When pure, they exert no action upon vegetable colors, but, on exposure to the air, become rancid and acid. They are inodorous when fresh, or at most, give off a faint, pe-

culiar smell, are insoluble in water, but very soluble in ether; and, when exposed to a strong heat, with free access of oxygen, they burn with a clear flame. Certain ferments resolve them into glycerine and fatty acids. Among these ferments are the putrid albuminous substances, and the pancreatic fluid.

Stearin (*stearate of oxide of lipyl*) is a pure white substance, crystallizing in snowy, glistening scales, which, under the microscope, appear as quadrangular tablets. It melts at 144°, solidifies without crystallizing; is brittle; when dry, a non-conductor of electricity, and yields stearic acid when saponified.

Margarin (*margarate of oxide of lipyl*) crystallizes in pearly needles, grouped in whorls; melts at 118°, dissolves slightly in alcohol, readily in hot ether, and separates from these solutions in pearly scales.

Olein (*oleate of oxide of lipyl*), or *elain*, is a colorless oil; solidifying at a low temperature; a non-conductor of electricity; becoming rancid on exposure to the air; never entirely free from margarin and stearin, and when saponified, yielding glycerine, oleic acid, and more margaric acid than the margarin mixed with it contains.

The usual method of obtaining these substances is to purify common fat by repeated meltings and washings in water, to dissolve this in boiling alcohol, and allow it to cool, when margarin and stearin separate in scales, and the solution contains the olein. Pure margarin is best obtained from those fats which do not contain stearin. Olein is sometimes obtained by digesting with half the saponifying quantity of potash; the stearin and margarin are saponified, and the olein remains unchanged.

Fats are widely diffused, not only through the animal, but also through the vegetable world. Some of these fats have been found isolated from the others, and crystallized.

In the human body, fat is always found in the *orbit of the eye*, around the *heart*, and among the *muscles of the face*, even after the most wasting diseases. It is also abundant in the *subcutaneous cellular tissue*, the *omentum*, the *female breast*, and about the *kidneys*. The *marrow of the bones* is only a liquid fat. The minimum of fat, and very often none at all, is to be found in the *pulmonary tissue*, the *glans penis*, and the *clitoris*.

In the fluids, it constitutes from 0.14 to 0.33% of normal blood. The *chyle* and *lymph* both contain fat, the former being very rich in it.

The period of life influences very much the deposition of fat. It is most abundant in childhood, less so in youth, and increasing again later in life. Women have more fat than men. Extreme activity of the sexual functions has been usually considered to diminish the amount of fat in the system. This is not the case in women, as it is well known that nearly all prostitutes, who do not destroy their health by ardent spirits, late hours, and the other excesses incident to their unhappy calling, have a decided tendency to *embonpoint.* Old maids, on the other hand, even long before the decay of their sexual functions, are noted for their leanness. Neither does the rule always, nor, according to most men's experience, generally, hold good with men. The most notorious rakes are often very fat, and those ascetics, who are known to be continent, are not found to be fatter than men who do not put such restraints upon their appetite. Short of actual diseased excitement of these functions, we do not believe that even the male sex is emaciated by their moderate exercise, unless, indeed, there should be some morbid tendency in the system which any indulgence may kindle into actual disease.

Great *muscular activity*, conjoined with a scanty or moderate diet, is sure to diminish the amount of fat. Temperament also exerts a powerful influence upon corpulency, and so do the states of feeling and the conditions of the mind. In diseases of a wasting character, and under any circumstances which interfere with nutrition, the fat is much diminished. In another class of diseases, it is increased, and pathological deposits of it take place.

It is undoubtedly true that the greater portion of the fat found in all animals is taken into the system preformed. In the carnivorous animals it occurs in abundance in their food, and in others, it has been found to exist in sufficient quantity in vegetables, to supply all that they contain. It is, however, also true that animals possess the power of forming it within their bodies from food which does not contain it, though where, when, or how this is done, has never yet been satisfactorily determined.

The uses of fat in the animal body are very numerous. Its beautifying property, the softness it communicates to the form, the agreeable plumpness, and exquisite flowing contour which result from it, will be best appreciated by comparing a young, graceful, well-developed woman with the thin, frail, perishing victim of consumption; or the plump, crowing, well-fed baby, with the poor emaciated little sufferer, that has been worn away with cholera infantum or marasmus. "How different," says Lehmann, "would be the appearance of the face, if all the fat were removed from the muscles, and from below the skin. The fat which smooths the bony corners and angles, and the narrow muscles of the face, is the cosmetic employed by nature to stamp the human countenance with the incomparable impress which exalts it far above all other animals."

Fat is also useful in equalizing pressure upon the external parts of the body; and we find, therefore, that it is deposited in greater abundance in those parts which are most subject to pressure, as the soles of the feet, and the buttocks. It also diminishes friction, and allows the muscles to glide over each other with facility.

When fluid, fat is a bad conductor of heat. Its diffusion, therefore, over the surface of the body, must afford a protection to the system from the extremes of temperature to which we are subjected.

Liebig has shown that fat subserves another important purpose in the economy, the maintenance of animal heat. Lehmann regards it as one of the most active agents in the metamorphosis of animal matter. He found a small quantity of it to be indispensable to the solution of nitrogenous articles of food during the process of gastric digestion. Still farther, it may now be regarded as a settled fact, that fat is the basis of organization, because the granules which lie at the foundation of all cell-metamorphosis, are themselves formed by the coagulation of albumen around globules of fat. Fat is also supposed to co-operate in the formation of the blood pigment.

The bile is formed in part from the fats of the body, and of the food. In the yolk-sac of the egg, it is well known that the fat of the yolk is in part converted into bile, to such an extent,

that the alcoholic extract of the entire yolk contains enough to be recognized by Pettenkofer's test. The blood of the portal vein, however, contains more fat than that of any other vein in the body, and this fat differs from the ordinary fat of the blood in being of a dark brown color, and very rich in olein.

"When animals are *starved* for any length of time, it is well known that they rapidly become emaciated; the urine still exhibits nitrogenous constituents, corresponding in amount to the products of effete tissue, while the gall-bladder is perfectly full, and the liver constantly pours out bile into the intestine, as I have convinced myself by a repetition of Magendie's experiments. The above fact seems to explain the cause of the bitter taste of which persons suffering from starvation very frequently complain. Whence can the liver extract the materials necessary to the formation of bile? The urine, although poorer in solid constituents, always contains a considerable quantity of urea; and the animal body contains few or no highly carbonaceous substances, with the exception of fat, which we here observe disappearing very rapidly, while at the same time there is an abundant secretion of bile.

"In *disease*, the diminution or increase of fat is inversely proportional to the secretion of bile. Polycholia, which seldom occurs in adults, but which, in children, constitutes the affection known as *Icterus neonatorum*, is always accompanied with rapid emaciation. In acute diseases, emaciation generally occurs in conjunction with critical symptoms, that is to say, when the organs of excretion resume their activity, and eliminate the materials that have become effete; hence the copious semi-solid feces. In all acute or chronic diseases of the liver, the fat accumulates either merely in the blood, or in the blood and in the cellular tissue. The obesity observed in habitual drunkards is not in consequence of their taking too much combustible into their bodies (brandy-drinkers, moreover, generally take only small quantities of solid food), but in consequence of the disturbed hepatic action, which the invariably abnormal condition of the liver, found after death, in these cases, proves to have existed."* Besides these facts, it has been found that in inflam-

* Lehmann's Physiological Chemistry, vol. i. p. 271.

mation of the liver, and indeed in any disease in which its functions are suspended, the fat in the blood is more increased than in any other class of diseases.

The *hydrated oxide of cetyl*, $C_{32}H_{33}O.HO$, the basis of *spermaceti*, occurs only in that fat; and, therefore, requires no special notice here.

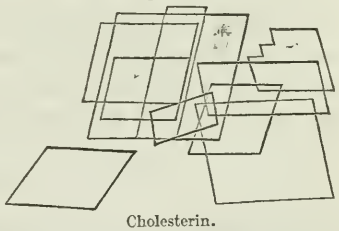
LIPOIDS.

Under this head are classified the non-saponifiable fats.

CHOLESTERIN.

This body separates from its hot alcoholic solutions in pearly scales, which appear under the microscope as thin rhombic tablets. It fuses at 296°, solidifying again in a crystalline form at 266°. It becomes electrical by friction, is insoluble in water, but soluble in nine parts of boiling alcohol, in soap-water, in the fatty oils, and in taurocholic acid. It is converted, by boiling with nitric acid, into a resinous mass and then into caproic, acetic, butyric, oxalic, and cholesteric acids. On dry distillation, it leaves a charcoal, and sends over an oily substance of a geranium odor.

Fig. 17.



Cholesterin.

Its formula is $C_{37}H_{32}O$. The products of its decomposition are three cholesterilines and two cholesterones.

It is best prepared by dissolving gall-stones containing it in boiling alcohol, filtering while hot, and purifying by repeated crystallizations from hot alcohol.

Small quantities of it are found in most of the animal fluids. It was first found in biliary calculi, and has since been discovered to be a normal constituent of all bile. It has also been found in the blood, in the brain, in pus, in the solid excrements, and in many products of disease.

Its origin is unknown. It must be formed in the living body, because it does not exist in the vegetable kingdom.

SEROLIN.

This substance was obtained by Boudet by extracting with hot alcohol blood which had been dried, boiled with water, and again dried. As the alcohol cooled, the serolin separated in pearly, glistening flocculi, slightly soluble in cold, freely in hot alcohol and in water. It contains nitrogen.

Of *castorin* and *ambrein*, we shall only say that one is a constituent of castor, the other of amber.

CHAPTER IX.

NON-NITROGENOUS NEUTRAL BODIES.

Most of these substances closely resemble one another in their empirical constitution, whence many of them have received a common title, "carbo-hydrates" or hydro-carbons. Their oxygen and hydrogen are combined in the same ratio as in water, and the number of their atoms of carbon is divisible by 6.

GLUCOSE.

This substance, the grape-sugar of the French chemists, is identical with diabetic sugar. It crystallizes in warty masses of minute rhombic plates. It is white, inodorous, sweeter than milk-sugar, not so sweet as cane-sugar; soluble in water, and slightly so in alcohol; insoluble in ether. Its aqueous solution turns a polarized ray of light to the right. It melts at 212°, and at 284° becomes converted into caramel, developing a sweetish odor. At a higher heat, it is charred.

In contact with nitrogenous bodies, it passes into lactic and butyric acids. With yeast, it ferments into alcohol. Nitric acid converts it into oxalic and saccharic acids; sulphuric acid browns it, but not so fast as it does cane-sugar; potash, boiled with it, gives it a fine brownish-red tint. Treated with caustic potash, and then with sulphate of copper, a blue solution is

formed, which gradually turns green and deposits a red powder. It forms a beautiful crystalline compound with chloride of sodium.

Its formula is $C_{12}H_{12}O_{12}$.

It is widely diffused through the vegetable kingdom, and may be prepared by the action of acids on other sugars, starch, woody fibre, &c. The ordinary method of obtaining it from diabetic urine is liable to the objection that it leaves acetates mingled with the sugar. Lehmann's plan is to evaporate it carefully till the whole residue is converted into a solid, yellowish-white mass, which is extracted first with absolute alcohol and then with hot spirit. From the latter, it is allowed to crystallize, and the mother-liquid is evaporated to facilitate farther crystallization.

Even this method, however, according to Lehmann, does not furnish this substance in a chemically pure state. To procure it totally uncontaminated by foreign ingredients, he saturates the aqueous solution of the alcoholic extract with chloride of sodium, crystallizes, dissolves the crystals in water, and cautiously precipitates with sulphate of silver. He evaporates the filtered fluid, extracts with alcohol, and crystallizes from distilled water.

The tests for *glucose* are fermentation, Trommer's test, polarization, and several others which the progress of science has shown to be totally untrustworthy.

Trommer's test is the reaction with potash and sulphate of copper. To employ it, the fluid is treated with *caustic potash*, filtered if necessary, it being understood that excess of potash does no harm, and then charged with a dilute solution of *sulphate of copper*, very gradually and carefully added to it. A precipitate usually falls, which is dissolved on stirring the fluid. After standing awhile, a pure red or yellow precipitate is formed. If the mixture be boiled, as commonly recommended, the color is not so fine; and, besides that, other substances also throw down the suboxide of copper when aided by heat, which do not effect this change when kept at the common temperature.

If but little sugar be present, it is best to evaporate to dryness, to extract with alcohol, and to apply the test to the watery

solution of the alcoholic extract. In searching for sugar in albuminous fluids, we must first neutralize with acetic acid, then evaporate, then extract with alcohol, precipitate the sugar by an alcoholic solution of potash, dissolve the precipitate in water, and apply the sulphate of copper to this solution. In this manner, the most minute portion of sugar will give a very distinct reaction.

The *fermentation test* is applied by adding yeast to a solution of glucose; carbonic acid is evolved, alcohol is formed, and the *torula cerevisiæ*, a microscopic fungus, makes its appearance in the fluid. It requires much familiarity with the microscope properly to apply this test; for urine, which contains no sugar, develops a fungus of the same form, differing only from the *torula* in size.

Fehling has applied Trommer's test to the *quantitative determination* of sugar. As modified by Dr. Day, his test solution is prepared as follows: Dissolve 69 grains of crystallized sulphate of copper in five times their weight of distilled water, and add to it first, a concentrated solution of 268 grains of tartrate of potash and then a solution of 80 grains of hydrate of soda in an ounce of distilled water. Put the solution into an alkalimeter tube, and add distilled water to make 1000 grain-measures of liquid. Every 100 grain-measures of this fluid is equivalent to 1 grain of grape-sugar.

For clinical purposes, the fermentation test gives sufficiently accurate results. The urine is weighed, and allowed to ferment at 99° in a Fresenius's alkalimetrical apparatus. After forty-eight hours, the whole is weighed, and the carbonic acid evolved estimated by the loss of weight.

Sugar is always found in the intestines after the use of vegetable food. It is found in the *chyle*, seldom in the *blood*, constantly in *eggs* and in the *tissue of the liver*. In the *urine* and in most of the *fluids*, it is found in diabetes.

Glucose originates from the digestion of amylaceous substances, and also, it is believed, from the metamorphosis of the protein compounds. Bernard finds that the liver can always be made to secrete in great quantities when the medulla oblongata, on the floor of the fourth ventricle, is irritated. It

has also been formed in undue quantities when respiration has been interfered with. Its use appears to be to act as a pabulum to the processes of oxidation which originate and keep up the animal heat. That this change is effected in the blood appears certain; and it is probable that the sugar is first converted into an acid, which unites with the alkali of that fluid and becomes a carbonate of the alkali, so evolving heat.

MILK-SUGAR.

Milk-sugar crystallizes in white opaque prisms or rhombohedra, containing two atoms of water. It is hard, craunches between the teeth; has a faint sweetness; is inodorous, soluble in water, insoluble in absolute alcohol and ether, and its aqueous solution turns the polarized ray to the right. Dilute sulphuric, hydrochloric, acetic, and citric acids convert it into glucose. Nitric acid changes it into mucic acid, with a little oxalic, saccharic, and carbonic acid; chromic acid produces from it both formic acid and aldehyde. It reacts with sulphate of copper and potash like glucose, and ferments, but not so readily as other sugars.

Crystallized, it has the same composition as anhydrous glucose; but, when heated, it loses water, and becomes $C_{10}H_8O_8$.

It is usually obtained by evaporating whey, and letting it stand a long time in a cool place to crystallize. The crystals are purified by recrystallization. Haidlen boils milk with one-eighth its weight of sulphate of lime, which coagulates the casein, filters, evaporates to dryness, removes the fat with ether, and extracts the sugar with boiling alcohol.

It is distinguished from glucose by the difficulty with which it dissolves in alcohol, the slowness of its fermentation in the presence of yeast, and its convertibility into mucic acid by the action of nitric acid.

It is determined *quantitatively* by Haidlen's process, just given; or, when more accuracy is required, by using Fehling's test on the alcoholic extract thus obtained.

This sugar is found in the milk of all mammalia. In woman's milk, its amount ranges from 3.2 to 6.24%, in cow's milk, it has

been usually stated to average from 3.4 to 4.3%, but Lehmann finds this too low. In asses' milk, it is rated at 4.5%; in mares', at 8.7%; in goat's, at 4.4%. In the colostrum, Simon found 7%, and in the milk six days after delivery only 6.24%. As nursing goes on, it continually diminishes, and neither *abundance* nor *insufficiency* of *diet* nor *disease* affects its quantity. Braconnot claims to have found it in the cotyledons of the seeds of plants.

Dumas and Bensch have shown that its quantity is increased by a vegetable diet, so that it is probably formed from the glucose resulting from the metamorphosis of starch, though when or how has never been determined.

The milk-sugar subserves in the infant organism the same purposes as starch and the other carbo-hydrates in the adult.

CHAPTER X.

PIGMENTS.

Nothing definite is known of animal pigments, so that they are classified according to color.

HÆMATIN.

This is usually regarded as the red pigment of the corpuscles, but it is unknown whether it is a product of metamorphosis of the true coloring matter of the blood, or whether we obtain it coagulated. Neither has it ever been isolated, in its soluble state, from the globulin. As obtained, it is a dark-brown, slightly lustrous, tasteless, inodorous mass; insoluble in water, alcohol, ether, or oils. It dissolves, however, in alcohol acidulated with sulphuric or hydrochloric acid, but not in water similarly prepared. The concentrated acids do not dissolve it, but only take up a little of its iron. The alkalies, however, dissolve it readily.

Digested in chlorine water, the iron dissolves as perchloride

of iron, and white flocculi fall, which Mulder regards as a combination of chlorous acid and hæmatin free from iron. Concentrated sulphuric acid deprives it of its iron, but does not affect its color nor alter its elementary composition.

Mulder's formula is $C_{44}H_{22}N_3O_6Fe$. The manner in which the iron is combined with the hæmatin is still unknown, notwithstanding the numerous hypotheses with which we have been favored. It has, however, been clearly proved not to be essential to the color of the hæmatin.

Hæmatin is obtained by treating blood with eight times its volume of a solution of sulphate of soda or of chloride of sodium, filtering and washing with the same solution. The residue is then dissolved in water and coagulated by heat. The coagulum is washed, dried, finely triturated, and boiled with alcohol acidulated with sulphuric acid, till the fluid passes through decolorized. It is now saturated with ammonia, when it deposits sulphate of ammonia and globulin. These are removed by filtration, the fluid evaporated to dryness, the solid residue extracted with water, alcohol, and ether, and again dissolved in alcohol saturated with ammonia. The solution is filtered, evaporated, and the residue extracted with water.

Hæmatoidin is a modified hæmatin found in certain extravasations of blood. It occurs in granules, globules, and jagged masses, as well as in crystals, presenting the form of oblique rhombic prisms.

Hitherto, hæmatin has only been found in the blood-corpuscles of the higher animals, in which it occurs as a viscid solution, mixed with globulin. The proportion of hæmatin in the corpuscles has been calculated at 5.72%, in the blood at 0.718%.

The origin of hæmatin is unknown. It is found in the thoracic duct, and has been supposed to be formed from the fat.

The function of hæmatin is equally obscure. While one set of experiments seem to show that it has an important relation to the aeration of the blood, others are equally pointed in favor of an opposite hypothesis. Virchow has shown that, during its decomposition, it passes into substances similar to if not identical with melanin and bile pigment.

MELANIN.

Melanin is obtained as a black, inodorous, tasteless mass or powder; insoluble in water, alcohol, ether, or acids, soluble in dilute solution of potash, from which it may be precipitated by hydrochloric acid. Nitric acid decomposes it, but chlorine does not. It conducts electricity, does not fuse, but burns in the air, leaving a yellowish ash, containing chloride of sodium, bone-earth, and peroxide of iron.

Scherer publishes, as the mean of three analyses, the following:—

Carbon	58.084
Hydrogen	5.917
Nitrogen	13.768
Oxygen	22.231
	100.000

The best method of obtaining it is by inclosing the choroid coat of the eye in a clean rag, and washing out the coloring matter.

Whether the black pigments, obtained from parts of the body other than the choroid coat of the eye, are identical with melanin, it is impossible to say at present. It is probably formed from hæmatin.

BILE PIGMENT.

There are two distinct modifications of the biliary pigment, which, however, under certain circumstances, seem capable of passing into one another. One of these, the *brown pigment*, the *cholepyrrhin* of Berzelius and the *biliphœin* of Simon, occurs as a reddish-brown, non-crystalline powder; inodorous and tasteless; insoluble in water, slightly soluble in ether, but more so in alcohol, to which it communicates a yellow tint; forming with caustic alkalies a clear yellow solution which soon changes to greenish-brown. The yellow solution, when treated with nitric acid, passes through the various tints of green, blue, violet, red,

and yellow again. Hydrochloric acid throws down from the potash solution a green precipitate, which seems to be identical with the green modification. Acids make it green, and chlorine bleaches it. It combines bases; and its combinations with the alkaline earths are insoluble.

The *green pigment*, the *biliverdin* of Berzelius, is insoluble in water, slightly soluble in alcohol, forming with ether a red solution, soluble in fats, in hydrochloric and sulphuric acids with a green color, and in acetic acid and the alkalies with a yellowish-red tint. Berzelius regards it as identical with the chloropyll of leaves. It is decomposed with extreme facility.

Fig. 18.

Bilifulvin.

Berzelius also found in bile some reddish-yellow crystals, to which he gave the name *bilifulvin*.

Its composition has not been settled. From 7 to 9% of nitrogen has been found in it.

Nitric acid is the usual test for it. When it exists in small quantities, it is precipitated with basic acetate of lead, and dissolved in alcohol, or diluted with sulphuric acid, to which it communicates a green tinge.

This pigment is found usually dissolved, though often only suspended in the bile. In the intestines it is very rapidly modified. The green tint seen in the excrements is very often decomposed blood instead of modified bile. In disease, it may be found in most of the solids and fluids of the body.

Its use in the body is unknown. Its origin is also obscure, though facts seem to point to hæmatin as its source; at any rate, recent observations appear to show that it is not formed in the liver.

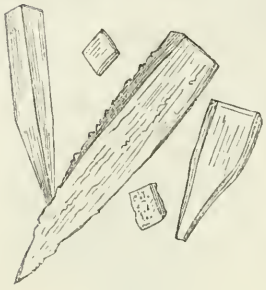
URINE PIGMENT.

Of this but little is known, owing to its extreme proneness to decomposition. Heller enumerates three pigments, *uroxanthin*, *uroglaucin*, and *urrhodin*.

Uroxanthin is a yellow pigment, which exists in solution in healthy urine and gives it its yellow color. It may be oxidized into uroglaucin and urrhodin.

Uroglaucin is a dark blue powder, which, when dried, has a coppery lustre, like indigo, and dissolves in alcohol with a fine purple color. It crystallizes in groups which are nearly black, but are blue and transparent at the edges.

Fig. 19.



Uroglaucin.

Urrhodin occurs in larger quantity than uroglaucin. It occurs in granules, which, under the microscope, have a fine rose-color. It is resinous, and burns with a clear flame.

Uroerythrin is the red coloring matter which appears in the urine in intermittent fever and some inflammations. It is a scarlet powder, inodorous, and almost tasteless; soluble with a faintly acid reaction in water and spirit.

In addition to these substances, a crowd of unexamined and unknown products are classified by chemists under the head of *extractive matters*. When this phrase is used, all that is meant by it is, that after the organic matters already described, and the various inorganic salts, have been removed from the tissues or fluids examined, there still remain certain nameless, unstudied bodies, which are soluble either in *water*, *dilute alcohol*, or *absolute alcohol*. They are divided into *water-extractive*, *spirit-extractive*, and *alcohol-extractive*, according to their behavior with the three above-named reagents.

BOOK II.

DIGESTION.

CHAPTER I.

PHYSIOLOGICAL RELATIONS OF DIGESTION.

It has already been said that, in examining the functions of the human body, we must necessarily proceed in a circle. They are all so completely dependent upon one another, the last result of one being the basis of the operations of another, that no satisfactory view can be obtained of any one of them, until the student have attained some general idea of the whole.

If, for example, we commence the study of the intellectual functions of man, we find it impossible to get any adequate notion of them by a mere subjective examination. The man who attempts to comprehend his mental acts by intellectual introspection alone, will be grievously at fault, because we know nothing of our spirits independent of the matter to which they are tied. The slightest changes in this, produce the greatest irregularities in them. The mind may be in a state of the highest activity, giving birth to the profoundest thoughts, and the most brilliant images, descending upon the sublimest ideas, and grappling with the loftiest themes; but, let a few drops of blood spirt out upon the delicate tissue of the brain, and all is over. The bright eye ceases to sparkle, the eloquent tongue to speak, and all that mental power that we have so much admired is as completely annihilated as though the mind itself had ceased to exist. A little lymph, effused upon the brain of an intelligent child, makes an idiot of him. A blow, which induces changes

not to be disclosed by the scalpel, the microscope, the test-glass, or any of our most refined and delicate modes of investigation, converts the gentleman into a ruffian, the saint into a reprobate, and the prude into a prostitute.

It is too late for the pure metaphysician to attempt to escape the force of these facts, by the assertion that the mind retains all its native force and activity, but that the shattered and ruined organs refuse to permit its manifestation. The day for assumptions and assertions has gone by, and the world demands proof instead of a bare *ipse dixit.* Such an unphilosophical wrenching of facts to fit a theory can no longer be permitted; and the more modest confession, that the Almighty maker has seen fit to yoke intellectual faculties and material organs in a manner as yet inscrutable to us, is at once nearer the truth, more appropriate in view of our immeasurable ignorance, and better adapted to promote the advance of science, which is, and always has been impeded by these stumbling-blocks of theories, that have been thrown in her way by her well-intentioned votaries.

The student of mental philosophy, thus driven to consider the physical framework of man, discovers that the mind and the body act and react upon one another in the most remarkable manner. He finds, on the one hand, that bodily states influence mental operations, and that the intellect and the feelings powerfully modify the functions of the body. Thus, a small amount of alcohol taken into the stomach brutalizes a man, and a suspension of the secretion of his liver or kidneys stupefies him completely, and suspends all his mental acts. On the other hand, a fit of rage gives him the jaundice, because this passion influences the secretion of the liver; grief arrests his digestion; fear depresses, hope stimulates his circulation, and mental anxiety impairs his nutrition and emaciates him. Thus the mind influences those functions which seem to be entirely withdrawn from its control.

If such close relations, therefore, subsist between the mind and the body, much more shall we expect to find the different functions of the body itself intimately connected with one another.

In considering this interdependence, it is difficult to fix upon a starting-point, because so many present themselves. If we inquire, however, what the ultimate object of human existence is, we shall have a very natural point of departure. No one will answer this question in any other way than by saying that man was designed to go on improving those distinctive faculties and powers, which place him at the head of animated nature. For this purpose he is endowed with the most exquisitely organized nervous system, and the most delicate apparatus of sensation. He is also furnished with a muscular system, capable of supplying all his common animal wants, and of aiding greatly in the development of his intellectual faculties. Thus, by those two modifications of common locomotive organs, the hand, and the apparatus of speech, he has acquired a capacity for almost endless improvement. Take them away from him, and science, art, indeed all mental culture would be simply impossible to him.

Physiologically, then, it is by the exercise of this nervous and muscular apparatus that man is to improve his intellectual powers. But we are so constituted that exercise is productive of waste. Life not only implies and involves death, but, by a strange but necessary paradox, it is death, death of the part which exhibits life. Does a muscle contract? Its little disks die by myriads. Does a nerve thrill with sensation? The nervous matter perishes, and we find its wrecks in the excretions. Does the brain act vigorously? The brain too, that portion of it, at least, which has been most active, dies and is swept away.

Now, it must be manifest that there must be some counteracting agency, or we should very soon wear ourselves out. This is supplied with a most liberal hand by nature. Through all these active organs meander countless vessels, which carry into them the fluid from which the shattered tissues are to be repaired, and others which convey away the ruins of the worn-out organs, that they may not clog the wheels of life. By a most admirable provision of nature, this activity which is so destructive becomes constructive also. The rapid changes which are going on produce an increased circulation through the part. Thus, more new matter is admitted, and the old is more rapidly hurried away. Life is too strong for its antagonist; and, so long as the

body is in health, the formative powers exceed the disorganizing. This we know, because all organs increase in bulk by exercise; and this could not be unless more matter is added to them by blood than is destroyed by their activity.

In consequence of this waste which is perpetually going on, the blood that is returning to the heart must necessarily be clogged with many impurities. These, if allowed to remain, would be most injurious to the economy, not only because they would by their presence diminish the vitality of the blood, but because also they must act as direct poisons to the organs with which they come in contact. Hence, an apparatus for the elimination of this effete matter must be provided. The various organs of secretion supply this deficiency. Excess of water and nitrogenous matters are carried away by the skin and the kidneys. Carbon is eliminated by the liver and the lungs, and the blood is thus carefully drained of its numerous impurities.

But even this is not sufficient. Oxygen must be introduced into the body, for the whole process of nutrition and elimination is, among other changes, a gradual oxidation. Through the lungs, therefore, and in part through the skin, this introduction is effected, and the constant chemical action between this atmospheric element and the organic contents of the blood, keeps up the animal heat which is essentially necessary to the due performance of the different functions of the organism.

It is manifest that in all these changes, the body is ultimately a loser. Every grain extracted and appropriated by the tissues is a grain lost by the blood. Not only all growth, therefore, but all the sustenance of the body must come from without. It is introduced as food into the stomach, and is there converted by the process of digestion into a pulpy mass, which becomes gradually more and more animalized as it penetrates the economy. The pultaceous mass which enters the intestines is gradually changed by the admixture of the secretions of the bowels and their accompanying glands. The feculent matter is separated from that which is nutritious, and this is gradually vitalized, and removed by the absorbents and bloodvessels. The changes still go on; granules, globules, and cells are formed, and

the new matter, thoroughly fitted for the uses of the economy, mixes with the blood and traverses the body.

Thus, all the functions are mutually dependent. Even that which is properly not the property of the individual, but rather of the species, the great function of reproduction, is not exempt from this general law of dependence. The phthisical mother brings forth phthisical children; the gouty father begets a gouty progeny. Care and attention, and comfortable circumstances for a series of generations are sure to produce a beautiful and vigorous race; while poverty, and labor, and servitude conjoined, and continued from father to son, certainly engender ugliness, deformity, brutality, and disease. No one can doubt this who takes the trouble to compare the handsome aristocracy and middle classes of Ireland with the extremely ill-favored peasantry of that unhappy island.

It might be said that the integrity of the whole body depended upon the soundness of digestion, but this would convey an erroneous idea, because it is a partial truth. The soundness of digestion is equally dependent upon the health of the system. While it is true that a foul stomach engenders headache and fever, it is equally true that disorder of the brain, whether structural or functional, or only a mental change, interferes with regular and healthy digestion. It must be borne in mind, therefore, when considering the influences which the stomach radiates outwards, that there are also influences radiating from every point of the periphery inwards upon it.

It is impossible to do more than glance at these numerous relations between the digestive cavity and the rest of the organs. After the *caveat* we have just entered, we may be permitted to say, without danger of being misunderstood, that any disturbance here affects the entire economy. The process of digestion, being that agency through which new matter is introduced into the system to supply the place of that which is wasted and carried off, must, if materially checked or arrested, put a stop to nutrition. A man, though fed on the most nutritious food, will starve as effectually when, from any cause, digestion is prevented, as though all food was taken from him.

When we examine the relations of the stomach with the dif-

ferent organs, we shall find that besides those remarkable changes which it induces in them, and which have received the name of sympathies, or sympathetic morbid phenomena, there are many other conditions of these remote organs which are dependent on the functional activity of the stomach.

A very close relation subsists between the great functions of digestion and respiration. Much of the food which we take is evidently respiratory; that is, it is plainly designed to proceed in the current of the blood to the lungs, there to be oxidated, and so to keep up the animal heat. An animal will starve as speedily when this sort of nutriment is taken from it, as when it is deprived of its albuminous aliment; and, indeed, it appears that the reduction of temperature, to which the man dying by starvation is subjected, constitutes very often the chief element in his pathological condition. In consequence of this intimate relation, irregularities of digestion are certainly productive of more or less pulmonary disturbance. *Dyspeptic phthisis* is not that figment of the imagination which some physicians profess to believe it, but a sad and very intelligible reality. There are many cases of tuberculous disease, which the watchful and observant practitioner, who has seen the case from the beginning, knows to originate in disordered nutrition commencing with imperfect digestion. There are many cases also in which an improvement in these great functions of nutrition and digestion has without doubt arrested the progress of the disease, even after it had committed notable havoc in the lungs.

The relations of digestion to absorption, sanguification, and nutrition are too manifest to demand any special attention.

The influence of this function upon the circulation is also very apparent. When it goes on regularly and well, the vessels are kept in that state of moderate fulness, and the blood in that due viscidity, which are best adapted to facilitate the transit of the nutritious fluid. Imperfections in the digestive process, independently of their sympathetic influence upon the circulation, through the medium of the nervous system, must necessarily change the natural consistence of the blood, and consequently the relations between it and the apparatus of the circulation, and in this manner, it must inevitably interfere with that function.

Its influence over secretion is equally well known. Unless it supply the materials for the secretions, they cannot be formed. Changes in digestion are sure to induce changes in the secretions. To mention but a single example, the urine, its deposits, and its calculi are known to be very much affected by the condition of the stomach, so that medicaments addressed to the latter organ will certainly affect the urinary secretion.

With innervation, locomotion, and reproduction, aside from the general influence it exerts upon them through the medium of the function of nutrition, and by sympathy, its connection is not distinctly understood. It may be that some of those obscure changes, which we now call sympathetic, may one day be traced to the direct chemical agency of depraved digestion.

CHAPTER II.

FOOD.

From what has just been said of the nature of the process of digestion, it is manifest that the food must contain all the chemical elements which enter into the formation of the tissues, or of the secretions. The inorganic substances, the soda, the potash, the lime, and the various mineral acids must come in, in this alimentary matter which we daily take into our stomachs. These materials are mixed with our ordinary food in sufficient quantity, and are disposed of by the system as fast as they are introduced. The organic matters must come from the same source, for we have already seen that the animal body is powerless to produce the majority of them.

That these organic compounds are all primarily derived from the vegetable kingdom, is manifest from what has already been said. In the human body, they may come from either the vegetable or the animal food we eat. Dr. Prout's classification of these substances being very convenient, and sanctioned, more-

over, by the high authority of Carpenter, will be here adopted, his aqueous group being omitted.

The first group is the *saccharine*, the members of which contain hydrogen, oxygen, and carbon alone, the first two in the proportion to form water. It includes not only the sugars, but all those vegetable substances, which, having an analogous composition, may be converted into sugar. As we have already shown, starch, gum, woody fibre, and cellulose possess this convertibility, and are therefore ranked with saccharine substances. Alcohol, into which sugar passes after fermentation, being a hydrated oxide of ethyl, is a haloid, and consequently belongs to the next group.

The *oleaginous group* includes all the oils and fats which enter into the food. Most, if not all of these, exist preformed in the vegetable kingdom; though, as we have seen, there are reasons for believing that these substances may be formed in the animal body as a result of the metamorphosis of tissue. The absence of nitrogen, the abundance of hydrogen and carbon, and the small quantity of oxygen to be found in these bodies, are their most striking characteristics.

The *albuminous* group is sufficiently characterized by its name. To it belong all the protein compounds which are contained in the food. The composition of the substances contained in it has already been described with sufficient minuteness under the head of histogenetic nitrogenous bodies.

The *gelatinous* group consists of gelatine, chondrin, and allied bodies, and is derived exclusively from the animal kingdom. There are a few alimentary substances which cannot be classified under either of these heads, which will be duly noticed as we proceed.

It is manifest from the composition of the sugars, that they cannot subserve directly the nutrition of the body. Either, therefore, they must undergo an intermediate metamorphosis, or they must discharge some other functions in the economy. Liebig has done very much for the philosophy of food by showing us that, while one portion is appropriated to the production of tissue, another passes directly into the blood in order to undergo oxidation, and consequently to generate heat. This

division into *nutritious* and *respiratory* food has been generally followed by physiologists, and seems to be established upon the firm foundation of fact.

Among the *respiratory* elements, the saccharine group stands prominent because of the quantity of carbon and hydrogen it contains. Those members of it which are not as yet sugars, are converted into it in the alimentary canal, while the sugars are directly taken up by the blood. The first step in the combustion, as it has been termed, appears to be the conversion of the sugar into *lactic acid*, which is thereafter oxidated and given off as carbonic acid and water.

Liebig has called attention to the amount of oxygen which enters the body, and the very small quantity that is retained. Thus, in the course of a year, an adult male takes in at his lungs, seven hundred and forty-six pounds of oxygen, and yet his weight is not at all or only very slightly increased at the end of that time. It must, therefore, have been given off as rapidly as it was received, and the products of the changes being examined, it becomes very apparent that it has formed a chemical union with the carbon and the hydrogen of the blood, which have then passed off in the form of carbonic acid and water. When we except that portion of the body which has thus been oxidated, this carbon and hydrogen are directly furnished by the food, and in great part by its saccharine portion.

But this is not the only purpose subserved by the saccharine aliments. They are undoubtedly convertible into fat, and that substance is by no means an unimportant element in nutrition and histogenesis. Lehmann has also shown that small quantities of sugar greatly promote the digestion of the true nitrogenous aliments, and that the acids resulting from the decomposition of this substance, discharge functions altogether distinct from respiratory changes.

The *oleaginous* group of alimentary substances is also classified by Liebig under the head of respiratory food, and we shall presently see, when we come to consider the phenomena of starvation, what an important relation they sustain to the function of respiration. It would, however, be an extremely imperfect view of the destination of this class of aliments, if we were to

suppose them entirely used up in the respiratory process. We have already seen that fat constitutes the basis of all granules and nuclei, and consequently of all cell-growth; that it plays an important part in gastric digestion, and assists in the formation of the bile. Thus, it is a very important element in nutrition, while at the same time, both it and sugar are totally incapable of supporting life of themselves.

Of the *albuminous* group we have already said enough under the head of histogenetic elements to show that it furnishes the true nutriment of the system. Albumen, or one of its cognate compounds, is the substance from which all the tissues are formed. It is remarkable, however, that alone it will not support life. When deprived of the flavoring substance, osmazome, it becomes so disgusting to the stomach, that it is rejected or not digested, and so, while possessing the necessary elements of nutrition, fails to nourish.

Dr. Prout has called attention to the fact that, in the only instance in which nature has supplied an animal with a single article of food for its nutrition, she has compounded it of substances belonging to these three groups. Milk contains *casein*, the representative of the albuminous, *sugar* and *butter* representing respectively the saccharine and oleaginous groups. The first of these substances furnishes the pabulum of the tissues, and, as it enters the young animal, carries with it a large quantity of phosphate of lime, in the most soluble form, thus furnishing the little creature with that earth which is to harden its growing bones, and fit them for the discharge of their functions. The *oily* matter of the cream and the *sugar*, dissolved in the whey, supplies those materials which are needed for respiration, and for the other purposes to which we have seen they are applied in the animal economy.

The *gelatinous* articles of food do not directly nourish even the gelatinous tissues, which are produced by the metamorphosis of the protein compounds within the body. It has been suggested that the hydrocarbon is eliminated through the lungs, and the azotized portion through the kidneys. Frerichs did not find any leucine or glycine in the urine after the injection of gelatine into the veins, but only an excess of urea. This class

of substances, therefore, seems to be useful only in its calorific capacity, so that the nutritive value of sups must depend wholly on the albuminous substances they hold in solution, and their property of keeping up the animal heat, by the combustion of the hydrocarbons of their gelatine.

The nutritive properties of food, so far at least as the formation of tissues is concerned, must therefore depend upon the amount of albumen ready to be assimilated, which it may contain. We say ready to be assimilated, for there is a great difference in the facility with which different substances enter the system. Food may contain the elements of nutrition in large quantity, but, owing to its nature, the manner in which it has been prepared, or the condition of the digestive organs, it may not be in a condition to be readily taken up. So, too, the calorific powers of different articles of diet cannot be estimated by the proportional amount of hydrogen and carbon they contain, but only by the quantity of these two elements uncombined with oxygen. Thus, sugar is not so powerful a supporter of animal heat as fat, for the simple reason that it has less of these elements in a state to combine with oxygen in the body. Liebig estimates the calorific power of fat to exceed that of any of the other articles of respiratory food. Thus, if it would require 100 parts of fat to keep up a given temperature a given length of time, it would demand for the same purpose 240 of starch, 249 of cane-sugar, 263 of grape-sugar, and 266 of spirits containing fifty per cent. of absolute alcohol. We may get a still clearer idea of this subject, if, assuming a definite number for the calorifying power of fat, we compare the other substances with it. Thus, then, if in such a table, we represent fat by 100, we should have for starch, 41.7; cane-sugar, 40.2; grape-sugar, 38; spirits, 37.6; and lean flesh only 13. From these facts, it is manifest that a *mixed* diet, that is to say, a diet which contains these various classes of alimentary substances, mingled in due proportion, is at once the most economical and the most agreeable to man.

"A nation of hunters," says Liebig, "in a limited space, is utterly incapable of increasing its numbers beyond a certain point, which is soon attained. The carbon necessary for respi-

ration must be obtained from the animals, of which only a limited number can live on the space supposed. These animals collect from plants the constituents of their organs and of their blood, and yield them in turn to the savages, who live by the chase alone. They, again, receive this food unaccompanied by those compounds, destitute of nitrogen, which, during the life of the animals, served to support the respiratory process. In such men, confined to an animal diet, it is the carbon of the flesh and of the blood which must take the place of starch and sugar.

"But fifteen pounds of flesh contain no more carbon than four pounds of starch, and while the savage, with one animal and an equal weight of starch, could maintain life and health for a certain number of days, he would be compelled, if confined to flesh alone, in order to procure the carbon necessary for respiration during the same time, to consume five such animals.

"It is easy to see, from these considerations, how close the connection is between agriculture and the multiplication of the human species. The cultivation of our crops has ultimately no other object than the production of a maximum of those substances which are adapted for assimilation and respiration, in the smallest possible space. Grain and other nutritious vegetables yield us not only in starch, sugar, and gum the carbon which protects our organs from the action of oxygen, and produces in the organism the heat which is essential to life, but also in the form of vegetable fibrin, albumen, and casein, our blood, from which the other parts of the body are developed.

"Man, when confined to animal food, respires like the carnivora, at the expense of the matters produced by the metamorphosis of organized tissues, and just as the lion, tiger, and hyena in the cages of a menagerie, are compelled to accelerate the waste of the organized tissue by incessant motion, in order to furnish the matter necessary for respiration, so the savage, for the very same object, is forced to make the most laborious exertions, and go through a vast amount of muscular exercise. He is compelled to consume force merely in order to supply matter for respiration.

"Cultivation is the economy of force. Science teaches us the simplest means of obtaining the *greatest* effect with the *smallest*

expenditure of power, and with means to produce a maximum of force. The unprofitable exertion of power, the waste of force in agriculture, in other branches of industry, in science, or in social economy, is characteristic of the savage state, or of the want of knowledge."*

There are cases, however, in which exclusive animal food is best adapted to the wants of man. Thus, the Pamperos of South America, who live in the saddle and hunt like tigers, live exclusively on beef, and thrive on it. So, too, the Esquimaux, in their cold, inhospitable climate, find the most suitable food to be the oily meat of the whale and seal. Again, in other portions of the world, an exclusively vegetable diet is both more agreeable and better adapted to the wants of the inhabitants.

Whether the food be obtained from plants or from animals, a due mixture of the albuminous, oleaginous, and saccharine aliments is necessary. When violent exercise is a man's common condition, the albuminous food ought to predominate in order to supply the deficiency caused by the rapid waste of the tissues. For the colder regions of the earth, excess of fat is necessary in order to supply the necessary materials for keeping up the animal heat which is so rapidly reduced by the low temperature of the air. The saccharine elements should preponderate in the diet of the resident in the tropics, who is sure to suffer from hepatitis if he neglect this simple precaution. In our own country much of the bilious disorder complained of proceeds from the quantity of highly carbonaceous food which is eaten during the summer time.

Besides these classes of food, fresh vegetables are necessary to health. A great deficiency or a total want of these is sure to engender that terrible scourge of the old navies, scurvy.

Deficiency of the *albuminous* articles of food is directly productive of debility, and all the diseases which follow in its train. Their excess leads to a plethora and the disturbances which attend that state of the system, such as apoplexy, active hemorrhage, inflammations, gout, &c. Deficiency of the *oleaginous* substances is thought to be productive of tuberculous and scro-

* Familiar Letters on Chemistry.

fulous disease. It is remarkable that Iceland is quite free from these diseases, an exemption to be attributed only to the amount of oily matters taken in the food. The marked improvement of tuberculous patients under codliver oil, for which it is believed most oils can be substituted, is thought by Lehmann to be accounted for by the fact to which we have already repeatedly referred, that oil-globules constitute always the first stage of cell-development. The body, failing to generate or separate fat from the common food, appropriates that which is directly introduced into the system, and thus derives at least a temporary benefit. Excess of these substances has already been cited as a prolific source of hepatic disease. When the *farinacea* are used in excess, without proper admixture of other matters, *rheumatism* is thought to be the method in which nature makes known the impropriety of this course.

The amount of food necessary for the support of a man must, of course, vary with the varying circumstances of habit, climate, and individual constitution. The more the system is wasted by exercise, the more albuminous food does it require, and this had better come from the animal kingdom, the food from which seems to enter more rapidly into the system, and to be assimilated with less difficulty than that from any other source.

Water is an essential portion of our ingesta. It is necessary to give the blood the proper amount of dilution, which is so important not only to the due performance of the function of circulation, but also to that of absorption, secretion, and nutrition. A certain degree of fulness of the vessels and a definite viscidity of the blood are essential conditions of health, and they are physical properties which depend entirely on the amount of water contained in the vital fluid.

The phenomena of starvation illustrate the views just advanced. Considered from a physiological point of view, it is the excess of waste over reparation. The chemist sees in it a gradual process of oxidation. The diminution of weight is caused by losses from all parts of the system, even from the bones; but those parts which suffer most are those which are most prone to this sort of disorganization. The fat and the blood, according to Chossat's experiments, suffered most.

The former lost 93.3, the latter, 75% of their weight, the whole body losing 40%. The most marked symptom of starvation is the disappearance of the fat, and this is not to be found either in the urine or the feces. It has passed off as carbonic acid and water through the skin and lungs. When it has gone, the pabulum of the lungs has been removed, the temperature of the body rapidly falls, the tissues are now attacked, and an offensive fetor is exhaled, indicative of the putrefactive processes which are going on within the body.

CHAPTER III.

GASTRIC DIGESTION.

THE food, such as we have described it, having been introduced into the mouth, and there masticated, and thoroughly mixed with the secretions of that cavity, the influence of which will be hereafter discussed, is propelled into the stomach, where it undergoes the first of that series of changes which is to assimilate it to the body it is designed to nourish.

The nature of digestion was very obscurely understood; or, more properly speaking, it was not understood at all by the older physiologists, who used to talk about concoction, and trituration, and a variety of other things, and tried to explain it upon any and every principle but the true one. It is now very generally understood to be a *chemical* process; under the control, indeed, of the vital powers, as are all other chemical processes in the body.

The solvent is the *gastric juice* secreted by the cells of the mucous membrane of the stomach, and to this we now call attention.

Various methods of obtaining pure gastric juice for experimental purposes have been suggested by chemists. Tiedemann and Gmelin used to feed dogs, or make them swallow irritants, and then kill them. In this manner, they obtained all the gas-

tric juice used in their experiments. Spallanzani and others made the animals swallow sponges attached to a string, and then withdrew them from the stomach. The objection to these methods is that there is an inevitable admixture of saliva with the fluid thus obtained. Of late years, this fluid has been obtained from fistulous openings in the stomach. Dr. Beaumont was the first to adopt this method. He procured the fluid for his famous experiments from the stomach of Alexis St. Martin, in whom such a fistula had fortunately been established by a gunshot wound. Since then, Blondlot, Bernard, Bardeleben, and others have established artificial gastric fistulæ in dogs, and drawn thence the fluid for their researches.

Bardeleben's method of establishing this fistula, to which Lehmann gives the preference above all others, is to make an incision two inches long from the ensiform process towards the umbilicus, exactly in the linea alba; to open the peritoneum an equal length, to seize the stomach, draw out a fold, pass a needle through it, make it fast to a peg laid across the wound, which is closed with sutures, taking care that the fold is contained in that portion of the wound nearest the navel, and then to wait for the sloughing of the stomach. This takes place from the third to the fifth day; the walls of the organ adhere to the sides of the wound, and the fistula is complete. Into this is inserted a small silver tube about three-fourths of an inch long, made fast by a couple of double hooks, and closed by a cork. It is remarkable that the health of the poor animals suffers but little from this torture.

Pure gastric juice is perfectly clear and transparent, almost colorless, having at most a pale-yellowish tint, and possessing a faint, peculiar odor, and a taste partly saline and partly acid. It contains a few gastric cells and nuclei, and some disintegrated molecular matter. Its reaction is strongly acid. It is not rendered turbid by boiling unless its free acid has first been neutralized. It very powerfully resists decomposition, and retains its digestive powers even after a vegetable mould has formed upon it.

Its specific gravity is but little higher than that of water, and it contains but a small quantity of solid matter. In dogs, this varies from 1 to 1.48%. In a horse, Frerichs found 1.72%; and

from some human gastric juice collected by Dr. Beaumont, Berzelius obtained 1.27% of solid constituents.

There has been much controversy regarding the free acid of the gastric juice. Some chemists have declared that it is hydrochloric acid, while others are equally positive that it is lactic, and Blondlot asserts that there is no free acid at all in this fluid, and attributes the reaction to the acid phosphate of lime. His reasons for this opinion are that he failed to dissolve carbonate of lime in the gastric juice, which ought not to have been the case if there were a free acid present. It has since been shown, however, that when the gastric juice is sufficiently concentrated, it will dissolve not only carbonate but phosphate of lime, and also iron and zinc, hydrogen being evolved, a solution which the biphosphate of lime is totally inadequate to effect. Dumas goes farther, and asserts that there is no biphosphate of lime to be found in the stomach.

Dr. Prout advanced the opinion that free hydrochloric acid caused this strong acid reaction. He distilled gastric juice, and, on precipitating the acid liquid which passed over with nitrate of silver, he obtained the chloride of that metal. Dunglison procured the same acid from Alexis St. Martin's gastric juice.

Many excellent observers, however, deny the presence of this acid, although there can be no doubt that it does pass over in distillation. Bernard and Barreswil account for this by supposing that hydrochloric acid, which, they say, passes over only towards the close of the distillation, is formed by the mutual reaction of the elements of the concentrated juice. They corroborate this opinion by the results of experiments on what they suppose to be analogous mixtures. Thus, when they distilled a solution of chloride of sodium with lactic acid, they found that, toward the close of the process, hydrochloric acid came over. Lehmann adopts very much the same opinion, and states that even when gastric juice is evaporated *in vacuo*, he has obtained as much as 0.125% of hydrochloric acid from the vapor that passed off. This, he thinks, is also produced by the same decomposition; and he finds, by experiment, that chloride of calcium, but not chloride of sodium, as Bernard and Barreswil assert, can be decomposed by evaporating it with lactic acid *in*

vacuo. Still farther, in objection to the hydrochloric acid theory, it has been urged by Bernard and Barreswil that oxalic acid throws down lime from the gastric juice, a reaction which cannot take place in a solution containing only the thousandth part of hydrochloric acid. Farthermore, starch, when boiled with hydrochloric acid, loses the property of becoming blue when treated with iodine, but lactic acid does not affect it. Starch, it is asserted, still strikes the blue tint with iodine, after being boiled in gastric juice.

That lactic acid is the acidifying principle, Bernard, and Barreswil, and Lehmann claim to have proved both directly and indirectly. The first-named chemists have found with the gastric acid, salts of lime, baryta, copper, and zinc soluble in water, a salt of lime soluble in alcohol and precipitable from this solution by ether, and a double salt of copper and lime of a deep color; all which reactions correspond with those of lactic acid.

Bernard attempts to strengthen this position by experiments on the results of the injection of different fluids into the blood. He finds that a food digested in gastric juice, and mixed with a very small quantity of hydrochloric acid, when injected into the veins, speedily destroys life. In experimenting on the salts of iron, in the same way, he found that the lactate was the only one which did not destroy life. It is difficult to see the bearing of such experiments as these upon the question; as the rude pushing of an injection into the veins can in nowise resemble the gradual process of absorption from the stomach and intestines. Besides, if we are to believe Wright's experiments, a fluid, like the saliva, which is daily introduced in large quantities into the stomach with perfect impunity, cannot be thrown into the veins without serious and even fatal mischief ensuing.

Lehmann has adopted a more practical method of deciding the question. He has separated the lactic acid and determined its quantity. Thus, in evaporating gastric juice to dryness *in vacuo*, he obtained from 0.098 to 0.132 per cent. of free hydrochloric acid from the vapor, and 0.320 to 0.583% of lactic acid from the residue; so that, if the acidity had depended exclusively upon this acid, there must have been from 0.561 to 0.908% of it in the gastric juice.

On the other side of the question, however, there is much to be said. Liebig denied the presence of this acid in the gastric juice, and asserted that its solvent powers were too feeble for it to be of any service if it were there. Enderlin, on examining the stomach of a recently beheaded criminal, failed to detect it, a circumstance to which Lehmann alludes with a perceptible sneer. To the *smell* of hydrochloric acid in fresh gastric fluid, alluded to by Professor Dunglison, but little importance can be attached. It is difficult for any one who has manipulated with hydrochloric acid, to understand how so minute a quantity of it, mingled with so much animal fluid, could be distinguished by the most acute nasal organs.

The most conclusive fact that has been adduced on this side of the question, is the analysis recently made by Professor Graham, of London. Dr. Bence Jones having procured some pure gastric fluid, submitted it to that distinguished chemist for examination. He proceeded by his method of "liquid diffusion," which is not liable to the objections that have been urged against distillation, and obtained free hydrochloric acid. Lactic acid was also present, but in small quantity.

Carpenter, in his *Principles of Human Physiology*, suggests that while lactic acid may be the solvent in the stomachs of dogs and pigs, the animals experimented on by the first-named chemists, it does not necessarily follow that it must also be the free acid present in human gastric fluid. Neither Lehmann, Blondlot, nor Bernard appear to have subjected the contents of a man's stomach to analysis, while it is upon human juices that Prout, Dunglison, Enderlin, and Graham have experimented. This may account for the discrepancy existing among such eminent observers. Both hydrochloric and lactic acids seem to be able to confer on gastric juice its solvent power, and to be capable of being substituted for one another; so that lactic acid may be the chief source of the acidity in the lower animals, and hydrochloric acid in man.

The solid residue of the gastric juice contains also *chloride of sodium* in abundance, *chlorides of calcium* and *magnesium* in smaller quantities, and traces of *proto-chloride of iron*. The latter may be recognized in strongly evaporated gastric juice by

means of ferridcyanide of potassium, and the former may be obtained in crystals, moistened with a yellowish syrupy mass, consisting chiefly of lactate of soda.

Phosphate of lime is present in small quantities in the filtered fluid. When much mucus or many cells are found in it, this salt exists in greater proportion. Alkaline sulphates and phosphates, and ammoniacal salts are not to be found in pure gastric juice.

There are also organic substances present in this fluid Among these are osmazome, and a substance soluble in water, but precipitated by alcohol, the *pepsin* or digestive principle. The ratio subsisting between the organic and the inorganic constituents, is a somewhat variable one. In the horse, Gmelin found 1.05% of organic, and 0.55% of inorganic constituents, and Frerichs discovered 0.98% of organic, and 0.74% of inorganic matters. In the gastric juice of the dog, Frerichs found 0.72% of organic, and 0.43% of inorganic constituents, while Lehmann obtained from 0.86 to 0.99% of the former, and from 0.38 to 0.56% of the latter.

It has been shown that an *artificial gastric juice*, which would digest food out of the body, can be formed, and that it requires a free acid and the mucous coat of a stomach, or a substance extracted from the latter, to confer upon it its full solvent power. The absence of either of these is fatal to the experiment.

Pepsin was first obtained and examined by Schwann, who found that, from the glandular structure of the stomach, he could separate a substance capable of forming a digestive mixture with acids, and of being precipitated by corrosive sublimate.

Wasmann afterwards examined it with more care, and confirmed Schwann's statement that it was obtained from the gastric glands. He carefully detached that portion of the mucous membrane of the pig's stomach, which contains the glands, extending from the greater curvature towards the cardiac orifice, washed it carefully, without cutting it up, and digested it in distilled water at a temperature of from 86° to 95°. This being poured off, removed many foreign matters. He then washed it again, digested it in about six ounces of cold distilled water, and washed it frequently till a putrid odor began to develop itself. He precipitated the transparent, viscid fluid, obtained by filtra-

tion, with acetate of lead or corrosive sublimate; freed it from the metal by means of sulphuretted hydrogen; washed it well, and again precipitated it with alcohol.

Thus obtained, it falls in white flocks, which dry to a yellow or gray, gummy, slightly compact, hygroscopic mass. After drying, it is but sparingly soluble in water, yielding a turbid solution, which still possesses the characteristic properties of this substance, though greatly diminished. In the moist state, however, it is readily soluble in water. Alcohol precipitates it from its watery solution; mineral acids first cloud the solution, and then, when added in slight excess, clear it up again. Metallic salts precipitate it imperfectly, ferrocyanide of potassium not at all, and heat does not coagulate it when it is entirely unmixed with albumen.

Lehmann objects to this mode of Wasmann's, that it never obtained the artificial gastric juice pure, but always mixed up with putrid substances and partly digested particles of food. He has, therefore, adopted the following method, which is given in his own language.

"The stomach of a recently killed pig having been properly cleaned, I detached from it the portion of mucous membrane in which the gastric glands chiefly lie.

As this piece of mucous membrane still contains a tolerably thick layer of submucous areolar tissue, or of the so-called vascular coat, in which the gastric glands are in a manner imbedded, this cannot be at once employed in the preparation of the digestive fluid, since then a quantity of digested gelatinous substance would be mixed with it. This source of error cannot be entirely avoided, since, in every mode of treatment, heterogeneous elements of tissue will be mingled with the glandular contents. In order, however, to obtain the latter in as pure a state as possible, the piece of mucous membrane, after being an hour or two in distilled water, at the ordinary temperature, must be gently scraped with a blunt knife or spatula; the pale, grayish-red, tenacious mucus which adheres to the blade, must be placed in distilled water, and the mixture must be kept at the ordinary temperature for two or three hours, being frequently shaken in the interval; a little free acid must then be added, and the mixture placed for half an hour or an hour in a hatching oven, at a

temperature of from 35° to 38°.* By this time, the fluid will be found to have lost much of its viscidity; it is now only slightly turbid, and it passes readily through the filter, in the form of a perfectly limpid fluid, with a scarcely perceptible yellow tint.

These and similar artificial mixtures are of much service, as experience has indeed fully shown, in the investigations of different conditions and phenomena in relation to digestion; but they are far less suited than the gastric juice discharged from the living animal for experiments, having for their object to isolate as much as possible from the unessential ingredients, and to render fit for chemical analysis, the true digestive principle, or the group of substances which constitute it. If the gastric juice from the living animal be always mixed with a little saliva, that fluid interferes far less with an accurate analysis than the albumen and the different peptones in the artificial digestive fluids; and even if we could separate the albumen, the peptones would still be associated with the digestive principle, as, indeed, they are even with the natural gastric juice, although in a far less degree. Notwithstanding the labors of many observers, it appears by no means impossible, that by repeated investigations we may so limit the digestive principle, as to find a chemical expression for it, whether we can exhibit the actual substance or not. Frerichs, in his classical article on digestion, has hit upon the right line of investigation, upon the only course which can lead to definite results, when he precipitated the natural gastric juice with alcohol; unless too much alcohol be added, the greater part of the peptones, and also of the aqueous extractive matter of the saliva, remains in solution, as indeed does a little pepsin. The precipitate dissolves pretty freely in water, from which it is precipitated by corrosive sublimate, protochloride of tin, basic acetate of lead, and tannic acid, and in an imperfect manner, by neutral acetate of lead; it does not become turbid on boiling, exhibits strong digestive properties when treated with dilute hydrochloric or with lactic acid, but, like the gastric juice, is deprived of them by boiling, by absolute alcohol, or by neutral-

* Centigrade equivalent to from 95° to 100.4° of Fahrenheit's thermometer.

ization with alkalies; in an alkaline solution it very soon becomes putrid, and in a neutral one, it seems to give rise to the formation of fungi; but when rendered acid, it remains a very long time without suffering decomposition, exactly as natural gastric juice. Frerichs has proved that the flocks, precipitated by alcohol, contain sulphur and nitrogen."*

It has been suggested by Professor C. Schmidt that the gastric juice is a true conjugated acid, hydrochloric acid being combined with pepsin, and that this compound acid forms soluble compounds with albumen, gluten, chondrin, &c. This pepsin-hydrochloric acid is, according to this chemist, decomposed at 212° into coagulated pepsin and hydrochloric acid, and it is impossible to reproduce it after the separation. When brought in contact with an alkali, pepsin is precipitated. He farther says that when an artificial digestive mixture has lost its power, it regains it on the addition of fresh hydrochloric acid. Under these circumstances, he thinks that the pepsin-hydrochloric acid is liberated from its compounds, and thus enabled to act upon fresh matter, while the albumen or other substance which was combined with it is taken up by the hydrochloric acid.

Lehmann objects to this hypothesis that he has failed to detect between the acid and the matters digested any of the ordinary relations between acid and base; and that these digested matters are altogether different from the substances originally introduced into the stomach.

"In regard to the solvent power of pepsin for coagulated albumen, it was observed by M. Wasmann, that a liquid which contains 17-10,000ths of acetate of pepsin and 6 drops of hydrochloric acid per ounce, possesses a very sensible solvent power, so that it will dissolve a thin slice of coagulated albumen in the course of six or eight hours' digestion. With 12 drops of hydrochloric acid per ounce, the white of egg is dissolved in two hours. A liquid which contains $\frac{1}{2}$ a grain of acetate of pepsin, and to which hydrochloric acid and white of egg are alternately added, so long as the latter dissolves, is capable of taking up 210 grains of coagulated white of egg at a temperature between 95° and 104°.

* Physiological Chemistry, vol. ii. p. 47.

"It would appear, from such experiments, that the hydrochloric acid is the true solvent, and that the action of the pepsin is limited to that of *disposing* the white of egg to dissolve in hydrochloric acid. The acid, when alone, dissolves white of egg by ebullition, just as it does under the influence of pepsin; from which it follows that pepsin replaces the effect of a high temperature, which is not possible in the stomach. The same acid, with pepsin, dissolved blood, fibrin, meat, and cheese; while the isolated acid dissolved only an insignificant quantity at the same temperature; but, when raised to the boiling point, it dissolved nearly as much, and the part dissolved appeared to be of the same nature. The epidermis, horn, the elastic tissue (such as the fibrous membrane of arteries), do not dissolve in a dilute acid containing pepsin. M. Wasmann remarked that the pepsin of the stomach of the pig is entirely destitute of the power to coagulate milk, although the pepsin of the stomach of a calf possesses it in a very high degree; from which he is led to suppose that the power of the latter depends upon a particular modification of pepsin, or perhaps upon another substance accompanying it, which ceases to be formed when the young animal is no longer nourished by the milk of its mother."* A portion of these views requires modification, as we shall presently see.

The amount of gastric juice secreted at any given time, and the circumstances which influence the activity of the glands, have been very carefully studied. From these, it would appear that the quantity actually secreted, amounts to from 60 to 80 oz. a day. This estimate is purely approximative, calculated upon the saturating capacity of gastric juice for albumen, and the amount of that substance assimilated during 24 hours.

The secretion of this liquid is influenced by a great variety of circumstances. Thus, mechanical irritation, within certain limits, stimulants, and salt, increase the activity of the secernent glands, and the quantity of the secretion. Cold at first diminishes the secretion of gastric juice, and afterwards increases it, apparently, in consequence of a reaction, analogous to that which is familiarly

* Graham, Elements of Chemistry.

known to take place on the surface after the application of cold. Moderate heat does not affect it, but a high temperature arrests the secretion, and brings on an adynamic condition which is speedily fatal. Disturbances of the nervous system, as anxiety, grief, fear, fever, &c., materially diminish the secretion.

It was, at one time, supposed that the nervous system controlled digestion, by stimulating secretion and absorption; and numerous experiments were made to prove that this influence was exerted through the pneumogastric nerves. It was generally believed that a section of these nerves entirely suspended the secretion of the gastric juice, so that the animals, upon which the operation was performed, died of inanition. Dr. Reid's experiments, however, proved that this was altogether too broad an assertion, as he found those animals that lived long enough, recovered gradually the power of secretion and absorption. The truth appears to be that, while these functions are greatly under the influence of the nervous system, they are by no means entirely controlled by it.

The result of the action of the gastric juice upon the food has been called *chyme*, but it is by no means a homogeneous mass. On the contrary, the food is partly dissolved, partly suspended in a state of very minute division.

The portion held in solution is not merely dissolved, but also materially modified. The food is changed, whether it be coagulated or not. New substances are formed out of the protein elements of the food, more soluble than those, and more easy of absorption. These have been called *peptones*, and they are formed by the action of the gastric juice without evolution or absorption of gas, and without the formation of any secondary substance.

Thus when albumen, in its soluble form, is introduced into the stomach, or treated with natural or artificial gastric juice out of the body, the first effect is that which would be produced by any other acid; the liquid is rendered turbid by a partial precipitation of the albumen. After awhile, however, if a sufficient quantity of the solvent have been used, the turbidity disappears, and, as the process goes on, the coagulable matter constantly diminishes, till, at last, the liquid no longer gives any

trace of albumen, when tested by heat, nitric acid, or any other reagent.

To this modification of normal albumen, Mialhe, who first investigated it, has given the name *albuminose*. It is, as we have already said, not coagulated by heat or nitric acid, and the precipitate thrown down by alcohol is redissolved in water. It is, however, precipitated by the metallic salts, by creosote, and by tannin. It now readily passes through the animal membranes, while albumen refuses to permeate them.

Fibrin undergoes a similar change, being converted into *fibrin-peptones*.

Casein, when introduced into the stomach in its soluble form, is coagulated. It requires a longer time to be dissolved in the gastric juice than most other substances belonging to the class of protein compounds, and it appears that its digestibility is in an inverse ratio with the firmness of its coagulation. Thus, according to Elsässer, the casein of woman's milk, which only coagulates into a sort of jelly, is more easily digested than the hard, curdy casein of cow's milk.

The remaining members of the albuminous group behave with the gastric juice like albumen.

Gluten and the members of the gelatinous group are converted into substances which closely resemble the peptones just described, in their physical, and in many of their chemical properties. The degree of their digestibility, however, depends very much upon their physical properties, areolar tissue being less digestible than gelatine, and tendon and cartilage being hardly dissolved at all, but passing away usually with the excrements.

All the peptones, in the solid state, are nearly tasteless and inodorous, of a pale yellow color, readily soluble in water, slightly in spirits, not at all in absolute alcohol. They are not precipitated by boiling, but only by tannic acid, and corrosive sublimate, and by acetate of lead if ammonia have been previously added. They combine readily with bases, whether alkaline or earthy.

Lehmann has never succeeded in obtaining them perfectly free from mineral substances. The proportion of sulphur, ac-

cording to him, is the same as in the substances from which they have been derived, and that too, in the same form. He can, indeed, detect no quantitative difference between these products and their originals in the food, and compares the change to the metamorphosis of starch into sugar, or of cholic into choloidic acid.

Digestion, or the digestive power of the gastric juice, is suspended by boiling, by saturating the free acid with an alkali or even with phosphate of lime, by sulphurous, arsenious, and tannic acids, by alum, and by most metallic salts. It is impeded by the addition of alkaline salts or by saturating the fluid with peptones or other organic substances. Water will partially restore to a fluid thus saturated its digestive power, and so will a free acid repeatedly added, provided it be suitably diluted with water, and be not in excess. Hydrochloric and lactic acid can alone constitute with pepsin an active digestive fluid. Fats, according to Lehmann, when added in certain quantities to the gastric juice, promote the conversion of the protein compounds into peptones.

Gastric juice exerts no influence whatever over *non-nitrogenous* articles of food. It will not, when rendered alkaline, alter starch into sugar, as Bernard supposed.

Of the abnormal constituents of gastric juice, little is known. In gastric catarrh, the common mucus of the stomach accumulates, and undergoes partial decomposition; generating, when mixed with saccharine and amylaceous food, acetic, butyric, and lactic acids. The formation of the last two are especially promoted by the presence of fat, giving rise to heartburn, &c.

"The contents of the stomach, in *post-mortem* examinations, and sometimes also the matters which are vomited in cases of gastric catarrh, are perfectly neutral or even alkaline on their outer surface, which is turned towards the walls of the stomach, while the inner parts often exhibit a very strong acid reaction. This phenomenon, wonderful as it appears at first sight, is obviously dependent on the circumstance that there must simultaneously have been a deficient secretion of gastric juice, and such slight movements of the stomach as not to have sufficiently mixed the contents with one another; and hence, either that

the inner portions have undergone one of the above-mentioned acid fermentations, or that they have retained the acid reaction peculiar to the food."*

After extirpation of the kidneys, *urea* is secreted by the gastric glands. Many authors assert that this substance has been formed in the stomach during Bright's disease. Lehmann has hitherto failed to detect it, though he has always found carbonate of ammonia. The only instances in which he has detected urea in vomited matters have occurred in hysterical girls who had been drinking their own urine.

CHAPTER IV.

INTESTINAL DIGESTION.

DIGESTION, as we have already seen, is not completed in the stomach. The farinaceous food is, in great part, untouched. The cane-sugar is unchanged, and the alteration of the fatty matters is scarcely perceptible. The pultaceous *chyme*, which passes out of the pylorus, is, as we have already said, composed of a solution of the peptones, holding the undigested matters in suspension. Much more remains to be accomplished before digestion can be considered as completed. The farther changes in the food occur in the intestinal canal, and can only be understood by studying the secretions that are discharged into that tube, and its contents after the various metamorphoses have been effected.

The principal secretions which will demand our attention are the bile, the pancreatic fluid, and the *succus entericus*, or intestinal juice, all of which exert an influence over digestion.

BILE.

Bile, when taken from the gall-bladder, usually occurs as a

* Lehmann, *op. cit.* ii. 51.

mucous, transparent fluid, capable of being drawn out in threads, of a green or brown color, a bitter but not astringent taste, with sometimes a sweetish after-taste, and an odor, which, on warming the fluid, often resembles musk. It does not diffuse itself readily through water unless the mixture be stirred; is usually alkaline, often neutral, and rarely acid. Mixed with mucus, it putrefies readily, but when that substance is removed, putrefaction is difficult to induce. Its specific gravity is about 1.02.

It has been procured for purposes of analysis and for physiological experiments, by establishing fistulæ, leading either into the *ductus communis choledochus* or into the gall-bladder. In either case, peritonitis is likely to set in and destroy the subject of the experiment.

The most widely different views have ever been held by physiologists and chemists, not only in regard to the functions of the liver, but also in reference to the nature of the bile itself. In our account of it, we shall follow Lehmann, who has himself been guided by Liebig.

All bile contains two essential ingredients, a resinous and a coloring matter. The resinous constituent is *glycine* or *taurine* conjugated with an acid. The coloring principle has already been described; it is combined with an alkali. Besides these, we always find in bile *cholesterin*, *fats*, and *fatty acids* combined with alkalies, as well as the various *mineral salts*, chloride of sodium, phosphate and carbonate of soda, phosphates of lime and magnesia, iron, manganese, but no sulphates of the alkalies. It is remarkable that the bile of salt-water fishes contains almost exclusively potash salts, while that of the herbivorous mammalia contains as great a proportion of soda salts. The presence of copper in this fluid has been already stated. Finally, mucus and epithelium are always mixed with it. The cells of the latter are the only morphological elements to be found in healthy bile.

Bile is so variable a fluid in different animals that we shall pay no attention to the quantitative examination of any but human bile.

According to Frerichs, normal human bile contains about 14% or a little more of solid constituents. Gorup Besanez found

9.13% of solid constituents in the bile of an old man, and 17.19% in that of a child of twelve years of age; but it requires farther investigation to determine whether the bile of the aged is always more dilute than that of the young. The organic constituents of human bile amount to about 87% of the whole solid residue. Of these, the alkaline taurocholates and glycocholates constitute by far the greater proportion, amounting to at least 75% of the entire solid constituents of this fluid.

Bensch and Strecker have shown that the bile of most animals contains a preponderating quantity of taurocholate of soda. As this salt ($NaO.C_{52}H_{44}NO_{13}S$) contains six per cent. of sulphur, the taurocholic acid, present in any given specimen of bile, is easily calculated from the amount of sulphur present in that portion of it which is only soluble in alcohol.

Berzelius obtained 12.7% of ash from ox-bile, the only variety of bile which has as yet been carefully examined for the determination of the inorganic constituents. According to Weidenbusch, it contains 27.7% of chloride of sodium, 16% of tribasic phosphate of soda, 3.025% of basic phosphate of lime, 1.52% of basic phosphate of magnesia, 0.23% of peroxide of iron, and 0.36% of silver.

According to Lehmann, bile contains preformed *alkaline carbonates*, the presence of which he demonstrates by exhausting in the receiver of an air-pump till it appears to boil, perfectly fresh bile, from which the mucus has been removed. After this, he saturates it with acetic acid, and by again surrounding it with a vacuum, very large quantities of carbonic acid are evolved. In 100 parts of fresh ox-bile he found, at one time, 0.0846, and at another, 0.1124 parts of simple carbonate of soda.

In normal human bile, Frerichs found from 0.20 to 0.25% of chloride of sodium, and an equal quantity of phosphate of soda.

There is a difficulty in determining the quantity of *mucus* in bile on account of the epithelium which is mingled with it. When this source of fallacy was removed as much as possible, Lehmann found 0.158 of mucus in human bile.

The abnormal variations of bile are numerous, but little understood. *Albumen* has been found in it, in fatty liver, in Bright's disease, and in the embryo. *Urea* occurs in it after

the extirpation of the kidneys, as well as in Bright's disease, and in cholera. It has also been found in the alcoholic extract of the bile of a man who died with fatty degeneration of the kidneys. Lehmann has found *sulphide of ammonium* in the bile of a child dying suddenly.

The solid constituents of the bile are diminished after severe inflammatory affections and dropsies, in typhus, diabetes, and often in tuberculosis. They are usually increased in those diseases in which the motion of the blood in the great vessels is diminished, as in disease of the heart, when the blood accumulates in the vena cava and the hepatic veins. In cholera, the same increase of density has been noticed.

Biliary calculi usually contain a preponderating proportion of cholesterin, many of them being formed exclusively of this substance, and a combination of the bile-pigment with lime. Rarely, carbonate and phosphate of lime are the principal ingredients. *Uric acid* is an occasional constituent of gall-stones. According to Bramsen, the formation of the majority of these concretions depends upon the separation of the combination of bile-pigment and lime already alluded to, which forms the nucleus of the calculus. The ratio of ash varies from 8.5 to 54.7%. Carbonate of lime, oxalate of lime, and the earthy phosphates have been found in the ash.

Mucus and epithelium generally yield the points around which the deposition of solid matter takes place. Pigment-lime is also found in the centre, whence it would appear probable that it takes a part in the formation of the calculus. It is unknown whether the bile around this crystallization point be healthy or not. At any rate, cholesterin and the pigment-lime are separated from their solution, and collected around this nucleus. An interesting question is suggested by these facts: what holds the cholesterin and the pigment-lime in solution in normal bile? This is answered by a very simple experiment. If the insoluble residue of a brown gall-stone be digested with taurocholic acid, or acid taurocholate of soda, it is entirely dissolved, with the exception of a few grayish-white flocculi, and the previously colorless fluid assumes the tint of fresh bile.

The *quantity* of bile secreted in a given time has been vari-

ously estimated by different observers. In the human subject, some have rated it at one ounce, others at twenty-four ounces in the twenty-four hours. Blondlot, from his observations on the flow of bile from fistulous openings established in dogs, estimated the secretion in one of these animals at from 40 to 50 grammes in the twenty-four hours, and calculated the amount secreted by man during the same time, at 200 grammes, or between 6 and 7 ounces. Bidder and Schmidt, who experimented on cats, state that when digestion is most active, that is, when biliary secretion is most abundant, one of these animals secretes 0.765 of a gramme, or 11.907 grains, corresponding to 0.050 or .772 of a grain in an hour; while, after ten days' fasting, it secretes, during the same time, only 0.094 of a gramme, or 1.249 grains, containing 0.0076 of a gramme, or 0.1173 of a grain.

The secretion is continuous, but augmented or diminished in accordance with the state of the digestion. It attains its maximum, according to the above-named observers, ten or twelve hours after a full meal, and then diminishes till twenty-four hours have elapsed. In prolonged starvation, its quantity gradually and progressively diminishes.

The same observers instituted a series of experiments on numerous animals, to ascertain the quantitative relation of bile to the other excretions. They first directed their attention to the excretion of carbon, and found that, "only from 1-10th to 1-40th of the carbon separated by the lungs is secreted in an equal time by the liver in the form of bile, so that at least 8-9ths or 9-10ths of the burned and expired combustible materials do *not* pass through the intermediate stage of bile, but remain in the circulating blood, where they become thoroughly oxidized."

The question of the *origin* of the bile, as Lehmann very properly observes, must necessarily precede all speculations on its physiological uses, because all theories of the use of this liquid necessarily either include or look back to its origin and mode of formation.

In investigating this subject, we are met, *in limine*, by the question: Does the bile exist already formed in the blood, or is

it formed from heterogeneous materials in the liver? Upon the answer given to this question, depends all our future opinions.

Lehmann, who, as we have already said, adopts the first-named opinion, argues from anatomical considerations as well as from chemical results. The direct intervention of so large a layer of cells, actively engaged in absorbing materials from the blood, between the smallest bloodvessels and the radicles of the bile-ducts, manifestly intimates that something more than mere transudation takes place in this organ; that a true metamorphosis of absorbed substances is effected within these cells. So, when Müller, and, after him, Kunde, extirpated the livers of frogs, the blood of the animals, when examined after several days had elapsed, gave no indications whatever of the presence of bile, which it ought to have done, did the liver merely separate from the mass of the circulating fluid a substance which already existed in it. When the kidneys are extirpated, urea is always found in the blood.

Lehmann farther calls attention to the peculiarity of the hepatic circulation. Every tyro in physiology knows that this organ separates its secretion from the blood of a vein, which is made up of radicles coming from all the chylopoietic viscera, the liver itself not excepted. This blood must necessarily be charged with nutrient materials, as well as with much excrementitious matter resulting from the disintegration of the organs whence it is derived. Provision is also made for detaining it some time in the liver, by spreading it out in a double set of capillaries, and thus not only increasing friction, but greatly enlarging the venous area of the abdomen in comparison with the space occupied by arterial blood. This remarkable anatomical structure is easily accounted for on the hypothesis of an active formation, and not the mere passive transudation of a secretion in the cells of the liver. In the former case, the time which is actually consumed in consequence of these arrangements, would be necessary to the perfect function of the cells.

It has been argued against this view that, during jaundice, bile is found in the blood, just as urea is discovered in the blood when the secretion of the kidneys is arrested. The phenomena of jaundice, however, have been too imperfectly studied, and its

causation is altogether too obscure to enable us to form from it any opinion of the method in which the liver acts. It is remarkable, also, that this affection rarely or never occurs in parenchymatous affections of the liver, in which the secreting power of that viscus must be annulled, whereas, it is very common in obstructions of the biliary ducts, and even in disorder of the duodenum. Such facts as these would seem to show that the bile is first formed, and then reabsorbed into the circulation.

The chemistry of the blood of the portal vein, as compared with that of the hepatic veins, will also throw light on this subject, although the present resources of organic analysis are too incomplete to solve many of the questions which arise during the progress of such an investigation. The intermixture of hepatic blood cannot be of much importance when we consider the small size of the artery as compared with the portal vein.

When the blood of the portal vein is examined, it is found that none of the most important constituents of the bile can be detected in it. It was at one time thought that Pettenkofer's test revealed the presence of the resinous acids, but when the source of the fallacy in olein and oleic acid, which has already been noticed, was removed, no such reaction took place. There is, therefore, no biliary matter in the blood of the portal vein, but it contains a remarkable quantity of oleic acid.

Lehmann's hypothesis that cholic acid is a conjugated acid, composed of oleic acid and a carbo-hydrate, has already been mentioned. This hypothesis derives support from the fact of the great quantity of olein contained in the portal vein, and the very small proportion of it which is to be found in the hepatic vein. The fat contained in the blood of these latter vessels is more consistent, and contains a larger proportion of margarin. There is also more fat of all kinds in portal than in hepatic blood, the former containing 3.225%, while the latter has only 1.885%.

The similarity of the reactions of oleic and cholic acids is another circumstance which gives probability to this view of Lehmann's. Kunde found that the fat of frogs, and indeed of all other fats which contain olein, whether they be derived from the animal or the vegetable kingdom, give an intense violet-

color with sulphuric acid and sugar, and that this reaction does not occur with any fats free from olein. This reaction differs from that of cholic acid, only in taking place more slowly and in requiring the presence of atmospheric air. There are, indeed, other substances which may give this reaction, but ordinary caution can avoid all error from these.

When the hepatic venous blood is examined, this test is only found to give a reaction with the ethereal solution. It has no effect whatever upon those matters soluble only in alcohol. These two parts furnish sufficient proof that there is no biliary matter whatever in hepatic blood.

The fact that less bile is secreted by fat than by lean animals proves nothing against this theory; for, as Lehmann observes, it is the very disposition to the deposition of fat which prevents them from using their oleaginous matters to form bile. They are fat because they do not form much bile; they are not deficient in bile because they are fat. Pathological observations confirm this view; for in cases of fatty liver, in which the hepatic cells are often dilated to twice their normal size with the excess of fat, the quantity of bile secreted is very much below the standard of health.

The occurrence of sugar in the liver has already been mentioned. Sugar is always conveyed to the liver, by the portal vein, during the digestion of vegetable food. This substance is always contained in the portal vein and its formative branches, and is rarely found in the chyle. Frerichs thinks that the sugar is contained in the parenchyma of the liver. By the loss of six atoms of water, the carbo-hydrogen adjunct of Lehmann (C_{12} H_6O_6) would be formed from the sugar, and thus cholic acid might be generated.

It appears from numerous observations that the fats and sugar are in an inverse ratio to one another in the hepatic and portal veins. Fat, as we have already said, predominates in the portal vein, sugar in the hepatic. Reasoning on this fact, we might conclude that the fat, during the progress of metamorphosis in the liver, had been converted into cholic acid and sugar. It has already been shown that, under certain circumstances, sugar might result from the changes of the protein compounds. Far-

thermore, the extractive matters may also furnish a portion of this liver-sugar.

Another interesting inquiry is whether the nitrogenous adjuncts of cholic acid, glycine and taurine, with which it forms glycocholic and taurocholic acids, exist preformed in the blood. The first substance has never yet been detected in the blood of the portal vein. Neither can taurine be discovered in portal blood, but it is settled that this blood contains more sulphur than that of the hepatic vein. On investigating the source of this sulphur, Lehmann found in portal blood a spirit-extractive very rich in sulphur. From this the taurine may in part be formed. The fibrin also, being greatly diminished in its passage through the liver, may furnish a portion of these nitrogenous adjuncts. The albumen is also diminished, and if it be supposed to enter into the formation of the new hepatic blood-cells, the walls of which contain no sulphur, another probable source of the sulphur of taurine is pointed out.

The *pigment* also is not to be found in portal blood; and, as has been already suggested, appears to be formed in the liver from hæmatin. "It appears no mere image of the fancy, to regard the speckled, distorted, irregular blood-corpuscles in the portal blood of fasting animals as cells that are growing old; for, at all events, we find that the blood-cells leaving the liver by the hepatic veins, exhibit precisely those characters which we ascribe to young blood-cells; hence, the cells of the portal blood do not undergo rejuvenescence in the liver, but suffer disintegration in that gland, and their remains are in part (the iron, for instance) applied to the formation of new blood-corpuscles, and in part converted into excreted matters; hence, it is very conceivable that the hæmatin loses its iron, and becomes converted into cholepyrrhin, which is mixed in the biliary canals with the other constituents of the bile."*

The *cholesterin* is a result of the general metamorphosis of tissue, and is found in the blood of the portal vein. The liver, therefore, can do no more than simply separate it from the blood.

* Lehmann, *op. cit.* ii. 96.

"The following may be regarded as a brief abstract of the above view regarding the origin of bile: While the non-nitrogenous and nitrogenous matters conveyed by the portal vein—most of which, even when in the blood, bear the character of substances in the process of metamorphosis—are applied to the formation of the biliary constituents, substances also pass into the bile which must be regarded as the residue or secondary products of the process which gives rise to the formation or rejuvenescence of blood-cells in the liver; in the latter class, we must especially place the fats and certain of the mineral constituents, while the nitrogenous substances, fibrin and hæmatin, are the most important members of the former. Hence, we do not regard the bile as the product of the metamorphosis of any single morphological or chemical constituent of the animal body (neither of the fat-cells nor of the albuminates); but we believe that several substances, chemically and morphologically distinct from one another, undergo alterations in the liver, and that their individual products unite in the nascent state, and thus form the compounds and admixture of substances which we find in the bile."*

As the bile descends in the intestines, it undergoes various metamorphoses, hereafter to be described, the results of which become gradually less and less, rendering it probable that its resinous portions are, as Liebig supposed, resorbed into the vascular system.

The long mooted question of the excrementitious character of the bile, can hardly be regarded as definitely settled. In the fœtus, the liver seems to be a depuratory organ; but, in the adult, if we are to allow the careful observations of Bidder and Schmidt to be conclusive, it would appear to have very little influence in this way. Besides this, there appears to be no vicarious action of the liver when the function of the lungs is impaired.

The influence of bile upon digestion has been by no means satisfactorily ascertained. The facts in reference to it are scattered, and have not yet been harmonized into an unobjection-

* Lehmann, *op. cit.* ii. 100.

able theory. The alkali of the bile does really unite with the strong acids of the chyme, in consequence of which the resinous acids of the bile are set free in the intestines, and gradually undergo their metamorphoses. Its digestive influence over fat and sugar, formerly asserted, has never been proved, and is generally denied, or limited to the power of finely comminuting the fat. Bernard has shown that it arrests fermentation, and others have observed that the contents of the intestines become completely putrid when they are removed from the influence of this secretion. Liebig has proved that its contents, especially the cholic acid, undergoes a gradual resorption in the intestines, and, passing into the blood, are oxidized in order to keep up the animal heat.

Lehmann regards bile as an incidental product of the action of the liver, the chief function of which he believes to be the formation, or at least the rejuvenescence of the blood-particles.

PANCREATIC JUICE.

This is a colorless, clear, slightly tenacious, tasteless, and inodorous fluid, with an alkaline reaction. Its specific gravity is 1.008 to 1.009. Its coagulum, formed on the application of heat, is inconsiderable, and acids and alkalies only render it slightly turbid. Bernard's description of the pancreatic secretion differs from the above account given by Frerichs and Lehmann. According to him, it is viscid and tenacious, and when heat is applied, the whole mass solidifies.

Its principal constituent is a substance resembling albumen or casein, but which is not perfectly identical with albuminate of soda, casein or ptyalin. Bernard calls it *chylopoine*. It coagulates imperfectly when heated, is precipitated by acetic acid, but redissolves slowly in excess of the reagent, especially if heat be applied, and from this second solution it is precipitated by ferrocyanide of potassium. Nitric acid precipitates it, and, if it be then boiled, especially if ammonia be added, a deep yellow color is observed. Chlorine water separates it in grayish flakes. Alcohol throws it down, but, according to Bernard, water redissolves it. It is to this substance that the secretion owes its

principal chemical and physiological properties. Frerichs found 0.309% in the pancreatic juice of an ass.

There are also found in this secretion a *butter-like fat*, *extractive*, and some *mineral* substances, consisting chiefly of carbonate and phosphate of lime and magnesia, chloride of sodium, and alkaline phosphates and sulphates.

Frerichs's analysis of the pancreatic fluid of the ass is as follows:—

Water	986.40	
Solids	13.60	
Fat		0.26
Alcohol extract		0.15
Water extract, albuminous (chylopoine)		3.09
Alkaline { chlorides, phosphates, sulphates }		8.90
Carbonate and phosphate of lime and magnesia		1.20
	1000.00	13.60

Valentin first showed that this secretion possessed the power of converting into sugar the amylaceous matters which have escaped the action of the saliva, and passed into the duodenum. Bernard and Frerichs have confirmed his opinion, and have shown that this secretion possesses this property in a higher degree than saliva.

Bernard has advanced the opinion, corroborated by numerous experiments, that the pancreas furnishes the means of digesting the fats. On killing a rabbit, shortly after giving it fat, he found the absorbents empty as far down as the duct of Wirsung, but, below that, filled with milky chyle. In another experiment, he tied the pancreatic duct, and found that the oil remained undigested in the intestines. He took the fresh juice from an animal, mixed it with fats, and found that it formed the same chyle-like emulsion out of the body as in it. These experiments of Bernard have been confirmed by the French Academy. They are farther confirmed by the pathological fact, that the diseases

of the pancreas are attended by the discharge of fatty matters *per anum*.

On the other hand, Frerichs, Lenz, and Bidder and Schmidt, have been unable to corroborate these experiments. After tying the pancreatic duct in cats that had fasted long, and killing them in from four to eight hours after the meal, they found the lacteals injected, and the receptaculum chyli distended with milky chyle. Frerichs tied the intestine far below the entrance of these ducts, and then, on injecting oil into the lower portion, found the lacteals in due time filled with milky chyle. Schmidt and Bidder, experimenting on butter, found that pancreatic juice, when not interfered with by gastric juice, did set free butyric acid, but that in the presence of the latter fluid, or of any acid, no such change took place. The same observers think that Bernard was led into error by not killing his rabbits soon enough. They found, on repeating his experiment of administering oil to rabbits, that when the animals were killed two hours afterwards, milky chyle, rich in fat, was found in the lacteals between the pylorus and the biliary duct. Later, the chyle gradually disappeared from the upper lacteals, and were found in those lower down the intestinal tract.

Most of Frerichs's experiments originated in a misconception of Bernard's views. He understood him to assert that a change into glycerine and fatty acids took place within the intestines; whereas, the Frenchman only intimates that such is probably the ultimate disposition of fat, and asserts that this change takes place out of the body, under the agency of the pancreatic juice; which statement we find confined by Bidder and Schmidt. Frerichs found that when the intestines were cut, and oil injected into either end, the lacteals proceeding from that portion which contained the bile and pancreatic juice were far fuller than those which came off from the lower bowel.

The result, therefore, of these counter-experiments, seems to be not so much a contradiction of Bernard's results, as a modification of them. They appear to indicate that his statements, while true in the main, are rather too broad, and that he has not given sufficient importance to the action of the bile, and of the *succus entericus* upon the fatty matters.

Frerichs thinks "that, as the decomposition of the bile is very much hastened by the pancreatic juice, this property is of some importance in effecting the rapid conversion of the bile into substances incapable of resorption."

INTESTINAL JUICE.

Recent researches on the chemistry and physiology of the intestinal juice have been made by Frerichs, Lehmann, and Bidder and Schmidt. Frerichs applied ligatures to the intestines of animals, so as to exclude food and all the secretions which are poured into the intestinal canal from above, and having returned the portions of intestine included in the ligature into the abdomen, and allowed some hours to elapse, he killed the subjects of his experiments. He found in the intestine a glassy, transparent, colorless, and tenacious mass, with a strong alkaline reaction. Lehmann obtained the same fluid from a fistulous opening in a man; and Bidder and Schmidt procured it from similar openings in dogs.

This juice does not mix readily with water; it cakes and seems to coagulate when treated with a saline solution, while the portion soluble in water behaves like mucus. Frerichs found from 2.2 to 2.6% of solid constituents in this juice, of which, the parts soluble in water amounted to 0.87%, the fat to 0.195%, and the ash to 0.84%. Lehmann found only 2.156% of solid constituents.

Frerichs could observe no digestive action whatever in the intestinal juice, but in this he differs from other observers. Lehmann, however, discovered that it possessed, in a very eminent degree, the power of transmuting starch into sugar, though he did not think it exerted any digestive influence upon the protein bodies, especially as cubes of coagulated albumen, and pieces of flesh introduced below the fistula in his subject, passed out of the rectum unchanged. Bidder and Schmidt, however, ascertained that the intestinal juice not only metamorphosed starch as rapidly as either saliva or the pancreatic fluid could, but also that the intestine exerts as powerful a digestive influence on flesh, albumen, and the other protein bodies, as the stomach. Bernard, too, attributes the same property to the intestinal juice.

He thinks that the mixed fluids, contained in the bowels, act the part of a *universal solvent* on all alimentary materials subjected to their influence.

CONTENTS OF THE INTESTINAL CANAL AND EXCREMENTS.

The examination of the contents of the intestinal canal has not led to any very certain results. The mixture is so heterogeneous, consisting of imperfectly digested food, indigestible matter, and the various secretions already described, in different stages of decomposition, that it is next to impossible to estimate the source whence any given product is derived, or to trace a single compound through its various metamorphoses.

The reaction of the contents of the bowels is acid in the duodenum and jejunum, but gradually changes and commonly becomes alkaline in the colon. Often, however, the contents next the mucous membrane are alone alkaline, the central portions being strongly acid. This reaction is partly due to the liberated resinous acids of the bile, but chiefly to *lactic acid*, the ultimate product of the metamorphosis of amylaceous matters in the intestines. These resinous biliary acids can be detected as low down as the ileo-cœcal valve. Sometimes *butyric acid* is found in the large bowel.

Grape sugar is also found in the intestinal canal. It is the result of the action of the pancreatic juice upon the food. A *protein body*, coagulable by heat, has also been detected. Lehmann is inclined to ascribe this to the transudation of some of the contents of the bloodvessels; but Frerichs thinks it results from a true digestion, or at least from the conversion of albuminose into ordinary albumen by the bile. *Dextrin* is rarely found, and only very small quantities of the *peptones*.

Biliary matters are always found in the alimentary canal. They have been discovered in the *gastric* contents of slaughtered animals and men suddenly killed. The lower down the contents of the intestinal canal are examined, the smaller is the quantity of the resinous acids of the bile which can be detected. In the duodenum, much unchanged bile is detected, but the acids gradually disappear, till, at the lower portion of the small intestines, nothing but cholinic and fellic acids and dyslysin can

be detected, and even these in small quantity. In the large intestine, even these have disappeared, and nothing remains but a little ethereal extractive. *Taurine* has been often detected by Frerichs throughout this tube. *Fat* is always found, and with it *cholesterin*. The *bile-pigment* gradually undergoes the same changes in the intestinal canal as are observed to take place during the putrefaction or decomposition of the bile.

The microscope detects in the insoluble matter, shrunken, fissured, and lobulated *starch granules; muscular fibres* in various stages of disintegration; and various *histological vegetable elements*, such as chlorophyll-cells, or those which contain the green coloring matter of plants, parenchyma-cells, spiral vessels, and sometimes yeast-cells.

The *gases* of the alimentary tube vary in their composition and origin. In the stomach, they often contain little in addition to atmospheric air, and these have probably originated from the gas contained in the saliva, or carried in with the food, or from atmospheric air swallowed during certain respiratory acts, the inspiration preceding vomiting, for example. Much of this gas originates from the fermentation of imperfectly digested food. If this be acetous, carbonic acid will be generated; if butyric, hydrogen will be developed. In 100 volumes of gas taken from the stomach of an executed criminal, Magendie and Chevreul found 14 volumes of carbonic acid, 11 of oxygen, 71.45 of nitrogen, and 3.55 of hydrogen. In gas taken from the stomach twenty-four hours after death, Chevillot found in two cases:—

Carbonic acid . . .	25.	27.8 volumes.
Oxygen	8.2	13. "
Nitrogen	66.8	59.2 "
	100.	100.

with mere traces of hydrogen.

In the *small intestines*, there is usually more gas than in the large. In these, Magendie and Chevreul found no oxygen, but nitrogen and a great quantity of carbonic acid and hydrogen. Chevillot found 2 or 3% of oxygen in this gas. Sulphuretted

hydrogen is often found in this gas, and its development is favored by the use of preparations of iron.

In the large intestine, gaseous accumulations are more common, and consist chiefly of carbonic acid, nitrogen, and carburetted with a small quantity of sulphuretted hydrogen. These gases usually proceed from putrefying food and animal juices, though there are some facts which seem to confirm the old notion of an ocasional *secretion* of gas from the walls of the intestine.

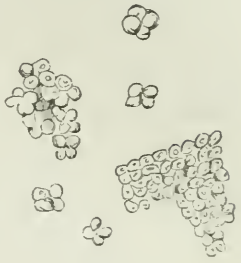
Vomited Matters.—These vary very much, in accordance with the ingesta, the time which has elapsed after taking food, and many other circumstances. When vomiting occurs shortly after eating, little more than unaltered food is rejected. When the food has remained longer in the stomach, the amylaceous matters undergo fermentation, either of the mucous, the acetous, the lactic, or the butyric kind. The vomit is then sharp and acid, in common parlance, setting the teeth on edge, except in cases of mucous fermentation, when the rejected matters are alkaline. In yellow fever, in cancer of the stomach, and other gastric hemorrhages, black or coffee-ground vomit takes place. This has been satisfactorily proved to consist of blood-corpuscles, altered by the juices of the stomach.

In *ileus*, from whatever cause produced, we have an inverted peristaltic action of the intestinal tube, and, of course, find its contents in the matters vomited. Bile is always thrown up during protracted vomiting. It is of no pathognomonic importance, for in the mechanical compression of the liver and the gall-bladder, and in the well-known increase of secretion from the glands connected with the alimentary canal which always attends nausea and vomiting, we have a simple and true explanation of this sort of bilious vomiting.

Goodsir has called attention to the fact that, under certain circumstances, which are not well understood, a microscopic *alga*, or infusorial plant, is thrown up from the stomach. This little organism is made up of square quadripartite cells, from 1-300th to 1-500th of a line in diameter, which are found either singly or combined in little plates. They resemble packets tied up, and from this resemblance they have received the name *sarcina*. Frerichs has studied their development and finds that

they originate from non-nucleated cells, isolated, or grouped in twos. These cells gradually undergo a constriction, which is crossed by another at right angles, till they appear to be divided into four equal parts. Each of these squares undergoes the same constriction, growing all the while, till at last each original individual expands into a large plate, intersected by rectangular lines, and easily divided into separate quadripartite cells. Lehmann thinks that it is identical with the *Merismopedia punctata* described by Meyen.

Fig. 20.



Sarcina.

The fluid of *pyrosis* has sometimes been found to be alkaline, and sometimes acid. Much diversity of opinion has prevailed in reference to it. It has been thought by some to be derived from the stomach, by others to come from the salivary glands. Wright long ago proved that it often originated in the latter organs, and Frerichs has since confirmed the observation. The latter chemist found that the vomited fluid contained sulphocyanides, that it digested starch, and, indeed, possessed the other properties of saliva.

In diabetes, *sugar* is vomited. The gastric glands probably possess the same power of separating sugar from the blood in this affection, which has often been noticed as belonging to the salivary gland.

Excrements.—The quantity of semisolid brown masses discharged, during twenty-four hours, from the rectum of an adult, living on a mixed diet, varies at from 4 to 6 ounces troy. As these contain about 25 per cent. of solid matter, the amount of solids, passing away in the feces, is from 1 to 1.5 ounces a day.

The insoluble portion of the feces consists chiefly of various morphological elements. We find in them fragments of undissolved muscular fibres, cartilage, and fibro-cartilage cells, elastic fibres, and the various vegetable structures already noticed.

We find, also, fat, crystals of cholesterin, and undecomposed food, as well as the brown bile-pigment, epithelium-cells, and

mucus-corpuscles. Various saline particles are also discovered by the microscope, among which are well-defined crystals of ammoniaco-magnesian phosphate. This salt was supposed by Schönlein to be pathognomonic of typhus, but it has been shown to occur in perfectly normal feces. In typhus, cholera, and certain forms of dysentery, however, it is increased in quantity, and its crystals are larger.

Dr. Percy has made several analyses of dry feces, which are recorded in *Simon's Animal Chemistry*. One of them, of the feces of a man eating the common food of England, we give:—

Substances soluble in ether (brownish-yellow fat) .	11.95
" " alcohol of .830 . . .	10.74
" " water (brown resinoid matter)	11.61
Organic matter insoluble in the above menstrua .	49.33
Salts soluble in water	4.76
" insoluble in water	11.61
	100.00

The ultimate analyses of the same feces gave, carbon, 46.20; hydrogen, 6.72; nitrogen and oxygen, 30.71; ash, 16.37 in the 100 parts. Enderlin examined the ash, and found it to consist of

Chloride of sodium and alkaline sulphates .	1.367	Soluble in water.
Bibasic phosphate of soda . . .	2.633	
Phosphates of lime and magnesia . .	80.372	Insoluble in water.
Phosphate of iron	2.090	
Sulphate of lime	4.530	
Silica	7.946	

This corresponds with Dr. Percy's statement, but Lehmann's results differ widely from these. He found in the ash of feces, 23.067% of soluble salts. It is remarkable that potash predominates considerably over soda. It is also worthy of observation that there is always a relative excess of magnesia over lime in the feces, as compared with the food.

The odor of the feces has been thought by some to depend upon the secretion of the glands of the colon, and by others, to

be due to the decomposition of bile. Liebig, however, has ascertained that, by fusing gelatinous and albuminous substances with potash, supersaturating with sulphuric acid and distilling, a fluid containing acetic and butyric acid, and possessing the peculiar fecal odor in an eminent degree, passes over. The odor varies with the article employed, but, in this way, every variety of fecal odor may be developed. The action of caustic potash at this high temperature, being only an imperfect oxidation, confirms Liebig's idea that the feces, like the soot in a chimney, are the product of the imperfect oxidation of the food. He calls attention to the fact that their odor differs from that of ordinary putrefaction or fermentation, and that, when they enter into fermentation themselves, out of the body, they lose this characteristic smell.

The small intestines in the fœtus, at the sixth month, contain a bright-yellow mass, composed of fat, salts, mucus, epithelium, and biliary matters. After the seventh month, the *meconium* appears. This substance contains cholesterin and other fats, epithelium and mucus, and a nitrogenous body. Lehmann could not detect bile-pigment or biliary acids, but Simon detected a notable quantity of both.

The bright-yellow, semifluid excrements of infants were found by Simon to contain a large amount of fat, much coagulated casein and bile-pigment.

A *green color* in the feces was formerly supposed to be always due to bile-pigment, though of late the presence of this coloring matter in the stools has been totally denied. As usual, the truth is found to lie between the two extremes. The green color may be present without any unchanged bile-pigment, but that pigment is sometimes found in green stools. In *calomel stools* sulphuret of mercury is always present, and this has given the green tint observed in experiments on intestinal mucus, which has led some persons to deny or doubt that this remedy stimulates the secretion of bile. But bile is also present, and may be recognized by Pettenkofer's test. Farthermore, Buckheim has ascertained, by observing fistulous openings in the biliary ducts, that calomel actually increases the amount of this secretion.

Iron also communicates a green color to the feces, especially

when it is taken in chalybeate waters. These stools, however, contain no bile, according to Lehmann, but owe their green tint to sulphuret of iron. That this substance is capable of producing this color may be shown by a very simple experiment. Add a proto-salt of iron to albumen; dissolve the precipitate in an alkali, and add to the solution an alkaline sulphuret. No precipitate takes place, but the liquid, till now colorless, assumes an intense "steel-green" tint. Many vegetable matters also stain the feces green.

The process of digestion commences in the *mouth*, as soon as the food has been introduced. There, the alimentary substances are mixed with the salivary ferment, which commences the transmutation of starch into sugar. There, too, the particles are comminuted so as to facilitate the action of the digestive fluids. There also they are mixed with atmospheric air, which furnishes the oxygen, so important to their farther transformation.

In the *stomach*, the albuminous flood is digested and converted into peptones, which are, in great measure, directly absorbed. Probably, all the sugar that is formed is also taken up and carried off by the gastric radicles of the portal vein to the liver, there to undergo the metamorphoses already glanced at. The fat, however, is only released by the digestion of the membranes which have enveloped it, and the farinaceous articles of food are little, if at all, changed.

In the *intestines*, the remaining changes are effected. There the insoluble and innutritious portions of the food are separated from the soluble and nutritious parts. The fat is there reduced into an emulsion, and the remaining amylaceous substances undergo their final changes. When the health is perfect, and the diet has been in proper quantity, nothing is finally rejected but those substances which are not fit to be taken up.

Thus, digestion is a complex process, requiring a thorough examination of all the cavities of the alimentary canal, since it is performed in them all, and not, as was formerly believed, accomplished in the stomach alone. As the mouth forms a subject of special study, the *digestive* processes there carried on will be considered in the description of that cavity, to which we now proceed.

BOOK III.

THE CHEMISTRY OF THE MOUTH.

CHAPTER I.

THE TEETH.

It is essential to every one who would deal properly with these beautiful organs, that he should understand not only their anatomical structure, but also their chemical relations to the various substances which surround them. Such knowledge as this, of course comprises the chemical constitution of the teeth themselves and of those fluids which constantly bathe them.

A consideration of the minute anatomy of the teeth, does not, of course, fall within the scope of a volume like the present; yet, as the chemical composition of the different components of these organs varies very considerably, a glance at their structure is necessary. Suffice it to say, that three distinct anatomical histological elements can be demonstrated in the teeth; the *dentine* or ivory, which consists of cylindrical and branching tubuli, and composes the bulk of every tooth; the *enamel*, which coats the exposed surfaces of these organs, and is arranged in hexagonal prisms; and, finally, the *cementum* or *crusta petrosa*, which contains lacunæ, and corresponds in all essential particulars with bone. In a perfectly healthy state of the teeth and gums, the enamel is the only one of these portions which, in man, comes in contact with the fluids of the mouth; but when, from any cause, the gums have receded, or the enamel has been worn away, the dentine is exposed to the same agents which should only operate upon the enamel. The *cementum* or *crusta*

petrosa is far removed from these influences, lying at the bottom of the fang. All these substances, of course, consist of animal membranes, holding earthy matters. A dilute mineral acid will dissolve out the calcareous salts, leaving the animal matter behind. It will then be observed that the enamel contains the least organic matter, the dentine considerably more, and the cementum most of all.

This will be seen by the following table from Von Bibra:—

INCISORS OF ADULT MAN.

	Dentine.	Enamel.	Cementum.
Organic matter . .	28.70	3.59	29.27
Earthy matter . .	71.30	96.41	70.73
	100.00	100.00	100.00

In this table, the cementum approaches so nearly to the dentine in chemical composition that there could hardly be said to be any difference between them.

Lassaigne, however, gives an analysis of cementum which differs widely from the above by Von Bibra. He finds in it—

Organic matter		42.18
Phosphate of lime . . .	53.84	57.82
Carbonate of lime . . .	3.98	
		100.00

Berzelius's analysis of *dentine* corresponds very closely with Von Bibra's. It is as follows:—

Cartilage and vessels		28.0
Phosphate of lime with fluoride of calcium	64.3	
Carbonate of lime	5.3	
Phosphate of magnesia . . .	1	71.7
Soda with chloride of sodium . .	1.1	
Loss		3
		100.0

Pepys obtained the same amount of organic matter, but less earthy matter than Berzelius, and a large amount of water. He

has, however, associated *water and loss*, so that it is difficult to determine what his actual results were.

Lassaigne found that the animal matter in the teeth gradually diminished as age advanced. We subjoin his table:—

	Organic matter.	Phosphate of lime.	Carbonate of lime.
Tooth of a child 1 day old	35.00	51.00	14.00
" " " aged 6 yrs.	28.57	60.01	11.42
" of an adult man	29.00	61.00	10.00
" of a man aged 81 years	33.00	66.00	1.00

Berzelius's analysis of enamel is as follows:—

Membrane, alkali, and water . . .	2.0
Phosphate of lime with fluoride of calcium .	88.5
Phosphate of magnesia	1.5
Carbonate of lime	8.0
	100.0

For the sake of a more extended comparison of the composition of the three organic elements of the teeth, we subjoin Von Bibra's analysis of the *incisors of an ox*:—

	Dentine.	Enamel.	Cement.
Phosphate of lime, with a trace of fluoride of calcium . . .	59.57	81.86	58.73
Carbonate of lime .	7.00	9.33	7.22
Phosphate of magnesia	0.99	1.20	0.99
Salts	0.91	0.93	0.82
Chondrin (glutin?) .	30.71	6.66	31.31
Fat	0.82	0.02	0.93
	100.00	100.00	100.00

By a comparison of two of Von Bibra's analyses, it would appear that the teeth of women contain more earthy and less organic matter than those of men; though, it must be confessed, no positive deductions can be drawn from so limited

a number of observations. The following is the analysis of a molar tooth of a woman twenty-five years of age:—

	Enamel.	Dentine and Cementum.
Phosphate of lime, with fluoride of calcium .	81.63	67.54
Carbonate of lime . .	8.88	7.97
Phosphate of magnesia .	2.55	2.49
Salts	0.97	1.00
Cartilage . . .	5.97	20.42
Fat	a trace.	0.58
	100.00	100.00

The corresponding analysis of the molar tooth of an adult man is here subjoined:—

	Enamel.	Osseous portion.
Phosphate of lime, with a little fluoride of calcium . .	89.82	66.72
Carbonate of lime . . .	4.37	3.36
Phosphate of magnesia . .	1.34	1.08
Salts	88	0.83
Cartilage	3.39	27.61
Fat	0.20	0.40
	100.00	100.00

A very slight consideration of the above analyses will show that all powerful acids will easily decompose the teeth, whether in or out of the body. The peculiar and very unpleasant sensation of "teeth set on edge," is induced in these organs whenever any strong acid is brought in contact with them, as they well know who have ever been so unfortunate as to have met with such an accident. The same sensation is also often produced by the acid contents of the stomach rejected in the act of vomiting.

Not only, however, have the mineral acids the power of dissolving out the earthy matter of these organs, but many organic acids possess the same property. The acids already spoken of as resulting from the decomposition of food, whether amylaceous

or albuminous, can dissolve the calcareous salts which make up the inorganic portion of the teeth.

The author has been engaged in a series of experiments upon these organs to determine the relative activity of these different acids; but, as yet, they have not been sufficiently numerous, nor have they been re-examined with sufficient care to warrant him in laying them before the public, at this stage of his investigations. This much, however, he may say, that so far as he has examined the subject, the different acids generated during the putrefaction or fermentation of vegetable or animal food, are fully capable of disorganizing the teeth. They convert the enamel into a white, opaque, very friable substance, almost entirely devoid of lustre, and soften the dentine so as to leave little but its animal matter. They materially diminish the weight of the teeth, in consequence of the earthy matter they have dissolved, which can be precipitated from the solutions by the ordinary reagents. Not satisfied with the examination of the individual acids, the author has also mixed finely comminuted food with the fluids of the mouth, and subjected the teeth to the action of the mixture while fermentation went on. The same results precisely were arrived at in this instance as when experimenting with the separate acids.

CHAPTER II.

SALIVA.

The importance of a thorough knowledge of the fluids of the mouth can hardly be overrated. They, of necessity, mingle themselves with all our ingesta, and exert, in this way, a powerful influence over digestion. Some of them hold important physiological relations with this function, and all of them may, in disease, materially interfere with its proper performance. None of them has a higher claim upon the attention of the physiologist

or the pathologist than the saliva, which it is our purpose to examine in the present chapter.

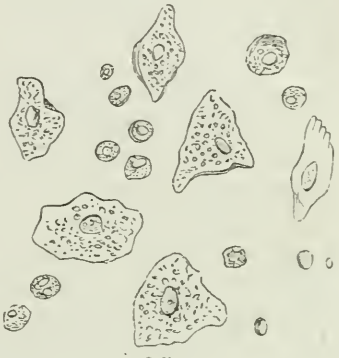
The name *saliva* has been as copious a theme for debate among the etymologists as the substance itself has been among the chemists. Some have derived it from *sal*, salt, because of the abundance of salts it contains, and for a variety of other reasons, which it would require too much time to particularize. Others will have it to be a corruption of σαλευω; and, if they are right in their etymology, it certainly is a degradation of this word, which was originally applied to the roll of the yesty waves of a troubled sea. Others take it from *salvando*, because it was thought to *save* life by curing a variety of diseases; and others, again, from *saliendo*, because it *leaps* into the mouth, from many little tubes, like the jets from a fountain. Some, again, think it a corruption of the Greek σιαλον, which is itself involved in similar etymological difficulties. Dr. Samuel Wright, of Edinburgh, is particularly learned upon this subject, and to his admirable papers in the *Lancet*, which we have very freely used, we refer the reader who is inquisitive about this little piece of etymology.

This name has been applied indiscriminately to the secretions furnished by the various glands which discharge their contents into the cavity of the mouth, the parotid, the submaxillary, and the sublingual, though we shall presently have occasion to show that these different organs do not produce a homogeneous liquid. The common saliva, besides being thus made up of different fluids, is mingled also with the buccal, lingual, and labial mucus. Various methods have been devised to obtain it perfectly pure. The most certain of these is probably to procure it from patients suffering under salivary fistula, though it has been doubted whether this can be taken as a normal secretion. Wright's plan was first to rinse the mouth with cold water; then, having depressed the lower jaw, to tickle the fauces so as to excite nausea without vomiting. This brings it out in a full stream, unmixed, as he thinks, with any foreign matter. The admixture of extraneous substances with the liquid thus obtained cannot, indeed, be great, but that some mucus must get access to it is manifest upon a moment's reflection. Epithelium scales and

mucus from the ducts must always be present, in whatever way it may be obtained, and to this we probably owe the globules, which the microscope detects in such quantities in the saliva. The time at which this fluid is obtained for examination, is by no means unimportant. Wright suggests that it be collected from a healthy person after a fast of about three hours.

Healthy saliva is described, by the last-named observer, as a "limpid fluid, having a faint-blue tinge, and a slight degree of viscidity. It is perfectly uniform in consistence, and unobscured by frothiness or flocculi. It possesses a faint sickly odor, *sui generis*, due to its constituent, *ptyalin;* this odor is strengthened by heat, and by most acids, but alkalies diminish and destroy it." Most observers assert that it is always totally tasteless, but Wright insists that it has a manifest sapor. He acknowledges that, to the individual secreting it, the freshly formed fluid is tasteless, but asserts that the saliva of another is always sapid, and that a man may retain his own in his mouth until it shall possess taste which becomes very distinct if it is collected in a vessel and then applied to the tongue. Lehmann and Jacubowitsch, the most recent writers on this subject, are at variance with Wright upon this point, and suggest that the saliva he experimented on may have been a little stale, a matter of some consequence in a fluid so prone to decomposition.

Fig. 21.



Saliva.

The *quantity* of this fluid, which is secreted in the course of a day, has never been exactly ascertained, and must be subject to great variation. The quantity of fluid ingested, the amount of motion in the muscles of mastication, the character of the substances taken as food, all must influence it. Movements of the jaws, stimulating condiments, even the thought of food increases its flow. Mitscherlich obtained from a patient laboring under salivary fistula, in the duct of Steno, about $2\frac{1}{2}$ ounces in

24 hours. At the same time he ascertained that the whole amount secreted was about six times the product of this single gland. It is probable, therefore, that this patient was making about 20 ounces of saliva in 24 hours.

Burdach calculates the amount at 8.2 ounces troy; Valentin assumes it at from 7 to 10.2; Donné fixes it at 12.5, and Thompson at only 6.7 ounces troy. Jacubowitsch found in dogs, that, in an hour, the two parotids secreted 49.2 grammes, the submaxillaries 38.83, and the rest of the glands, with the mucous membrane, 24.84 grammes. Lehmann observes that these observations of Jacubowitsch are not of much value, because he does not state the size or weight of the dog experimented on. The important fact ascertained by this observer is, that though the actual amount of the secretion may vary, because the water varies, the solid constituents separated by the three sets of glands are very much the same; the solids hourly discharged by each pair of glands amounting to about 0.232 of a gramme (3.581 grains), of which 0.080 (1.235 grains) is organic, and 0.152 (2.346 grains) in organic matter.

Bidder and Schmidt have made experiments on dogs which are not open to the objections urged by Lehmann. From one of the ducts of Wharton of a dog weighing about 35 pounds, they obtained, in an hour, 87.048 grains of saliva, so that the two submaxillary glands must have secreted 174.096 grains in the same time. From one of the ducts of Steno, they obtained, in the same time, 135.265 grains of clear, limpid secretion, so that the two were separating 270.53 grains an hour. The flow of saliva was stimulated by occasionally applying a feather, moistened with acetic acid, to the mucous membrane of the mouth. Assuming, now, that a man weighs 140 pounds; that is, four times as much as the dog, and that the secretion varies directly with the weight, he will secrete from his submaxillaries about 1.45, and from his parotids about 2.25 ounces troy in an hour. This would make the entire daily secretion amount to more than 6 pounds. Bidder and Schmidt think the actual amount to be about half this quantity. By actual experiment, they found that a man secreted from 3.2 to 3.9 ounces troy in an hour,

which would make the daily yield, deducting for sleep, about 3 pounds.

These estimates are, of course, approximative only, the actual secretion varying much, with extraneous circumstances, as we shall hereafter show.

The *specific gravity* of saliva is another point upon which observers are not unanimous.* The discrepancies here are very great, and are partly due, undoubtedly, to the greater or less admixture of mucus with the fluids tested by different authors. Wright's experiments, however, which are entitled to the utmost respect from their number, having been made upon more than five thousand individuals, and, from the accuracy and candor of their author, show that, even in perfect health, the density of saliva varies greatly, in consequence of idiosyncrasy, the nature of the ingesta, and a variety of other circumstances. He found it always denser after a meal than before it, in the evening than early in the day. It is "commonly thickened by an abundant use of animal diet, by fatty food especially, and by oily fish. Oysters and vegetable diet produce an opposite effect. I tried the specific gravity of the saliva in a healthy man for a week, and found its extremes to be 1.0079 and 1.0085. I then kept him upon vegetable diet and water for a week, during which time the lowest sp. gr. of his saliva was 1.0039, and the highest 1.0047. Throughout the following week he took nothing but animal food and water, with four ounces of bread daily; and the extremes of the sp. gr. of his saliva were 1.0098 and 1.0176. All alcoholic stimulants have a tendency to thicken the saliva; and, in large quantities, they not only alter its consistence, but materially diminish its activity. Moral emotions, variations in the state of the weather, electrical conditions of the atmosphere, light, sound, and other contingent

* The following are some of the estimates of different authors. Haller states it at 1.045; Lamure at 1.119; Siebold at 1.080; Thomson at 1.0038: Tiedemann and Gmelin at 1.0043; Mitscherlich at 1.0061 and 1.0088; Golding Bird at 1.0091; and Wright at 1.0079. Lehmann reckons it at from 1.004 to 1.006, and says it rises during health to 1.009, or sinks to 1.002. Jacubowitsch makes it 1.0026 before filtration, and 1.0023 afterwards.

circumstances, exert a remarkable influence upon the secretion of saliva, and also upon its specific gravity. Hence the difficulty of making accurate observations concerning it." Lehmann attributes the higher density which Wright obtained, to the greater use of animal food by the English.

Its reaction has also been a subject of discussion. Wright believes that alkalinity is essential to the proper performance of the physiological function of the saliva. He found the alkalies to vary from 0.95 to 0.303 per cent., a proportion which may, however, be considerably increased. If, at any time, it should exceed one per cent. he regards it as an evidence of disease.* He observed a remarkable connection between this secretion and the semen, a fact of no little interest, if we connect with it the well known pathological sympathy between the parotid gland and the testicles in mumps. After *coitus* in dogs the alkalinity of the saliva was notably diminished, and in both man and animals it is generally increased by abstinence from sexual intercourse. It is also increased during digestion and diminished in fasting. In the latter state, the saliva sometimes becomes acid, especially if the abstinence be protracted, but in moderate fasting (*e. g.* from 6 to 12 hours), Wright says the fluid may become neutral, but should never be acid. When, from admixture of mucus or other causes, it exhibits a reaction of this character, he suggests that some spirit or pepper be taken in the mouth, under the stimulus of which, in a *healthy person*, the quantity of alkali is always very much increased. He says he has known the proportion of alkali to be increased during the space of a quarter of an hour from 2 to 1.9 per cent. by the

* From Wright's method of stating this, it is manifest that he supposes the alkaline reaction of the saliva to depend upon the presence of free soda; but, as Lehmann remarks, in the saliva of graminivorous animals there is always much potash, and also a large quantity of lime, which is expelled from its combination with non-acid organic substances by the weakest acids, even by carbonic acid. Now, as it requires about 1.28 of sulphuric acid to neutralize one part of soda, we can easily make the statement in a manner which shall express the facts without committing us to any theory. This would be, that it usually requires from .122 to .388 parts of sulphuric acid to neutralize 100 of saliva, and that, should this amount increase to 1.28, we may suspect disease.

local application of an irritant. Slowness of digestion from the presence of much fatty matter, alcohol or vinegar in the stomach is, in like manner, accompanied by a decided increase in the quantity of alkali. Frerichs found that in a man smoking tobacco, the quantity of alkali was so much diminished, that it required but .15 gramme sulphuric acid to neutralize 100 grammes of saliva.

Mitscherlich was the first to isolate the saliva of one of the glands. He examined the fluid collected from the parotid at a fistulous opening in the duct of Steno. Since his time it has been examined by Vansetten and Garrod; and Magendie and Claude Bernard have investigated the fluids of the different larger glands, which they obtained from their own persons, by introducing tubes into the different ducts. These same observers, together with Jacubowitsch, Lehmann, and Bidder and Schmidt, have made the same investigations upon the saliva in the lower animals. From these experiments it is manifest that the secretions furnished by the different glands differ widely from one another in chemical composition and in physiological use. That from the parotid and sublingual is clear, limpid, and thin, while that from the submaxillary is thick and viscid, resembling simple syrup both in color and consistence.

The specific gravity of the *parotid saliva* is stated by Golding Bird at 1.0075. In dogs, Jacubowitsch found it to vary from 1.004 to 1.0047; and in horses, according to Lehmann, it ranges from 1.0051 to 1.0074.

Its reaction is usually alkaline during a meal, acid when fasting. This statement, which was first made by Mitscherlich, has been confirmed by Marshall and Garrod. These latter observers are inclined to attribute this to the rapidity of the discharge during a meal, and the slowness with which the secretion is formed at other times. They found that ordinarily but two or three drops were discharged by one parotid gland in a quarter of an hour, and that this was acid; but that in half a minute after a morsel had been taken into the mouth, the reaction was neutral, and, within the minute, alkaline. This continued till about twenty minutes after the meal, when it again became acid. This is accounted for by the fact of the general acidity of the

mucous surfaces of the mouth, which is sufficient to overpower the feeble alkalinity of the saliva, when secreted in small quantity. When the flow, however, is increased, the saliva more than neutralizes the mucus, and hence we have the alkaline reaction. The mucus, in cases of parotid fistula, comes, of course, from the lining membrane of the ducts.*

Upon what does this reaction depend? Shultz supposed it to be caused by ammonia. This is, however, impossible, because the fluid distilled from saliva is not alkaline, because saliva evaporated at a high temperature, is increased and not diminished in alkalinity, and because test-papers discolored by it, do not regain their original tint when heated. These phenomena are incompatible with the hypothesis of a volatile alkali. Wright, Garrod, and others, supposed it to depend on free soda, mainly because potassa could not be detected in it. The opinion, first broached we believe by G. Owen Rees, in his paper on Saliva, in the *Cyclopædia of Anatomy and Physiology*, that the tribasic phosphate of soda is the cause of this reaction, appears to be gaining ground. Strength is given to it by the generally acknowledged fact that the same salt communicates alkalinity to serum.

The composition of parotid saliva does not differ much from that of the common fluid. Like the latter, it contains *ptyalin*, extractive matter, sulphocyanide of potassium, epithelium, and mucus corpuscles, a volatile acid of the butyric group (probably caproic) combined with potassa, chlorides of sodium and potassium, a small amount of phosphates, and a trace of alkaline sulphates. Lime is also present, sometimes as a carbonate, but oftenest in combination with organic matter.

The saliva of the *submaxillary gland*, according to Jacubowitsch has a specific gravity of 1004.1, a less strong alkaline reaction, and less combined organic matter than parotid saliva.

A number of experiments have recently been made at Dorpat, by Jacubowitsch, under the direction of Bidder and Schmidt, to determine the chemical and physiological differences among the different salivary secretions of dogs. He determined the constitution of

* Mitscherlich found that it required .223 of sulphuric acid to neutralize 100 of parotid saliva.

A. Their ordinary or mixed saliva;

B. Their saliva, excluding the parotid secretion;

C. Their saliva, excluding the submaxillary secretion;

D. Their saliva, excluding the parotid and submaxillary secretions;

E. Their parotid saliva; and

F. Their submaxillary saliva.

The following are the results yielded:—

	A.	B.	C.	D.	and	E.
Water	989.63	990.48	988.1	996.04	991.45	995.3
Solid residue	10.37	9.52	11.9	3.96	8.55	4.7
	1000.00	1000.00	1000.0	1000.00	1000.00	1000.0
Epithelium, Soluble organic matter	3.58	4.25	2.24 / 5.04	1.51	2.89	1.4
Phosphate of soda, Chloride of potassium, Chloride of sodium, Sulphocyanide of potassium	5.82	4.08	4.20	—	4.50	2.1
		—	—	—	—	—
Phosphate of lime, Phosphate of magnesia	0.15	1.19	0.42		1.16	—
Carbonate of lime						1.2
	10.37	9.52	11.90	1.51	8.55	
						4.7

All these different secretions coincide in being unaffected by nitric, hydrochloric, sulphuric, phosphoric, and acetic acids, and by solutions of ammonia and alum; in being only rendered slightly turbid by ferrocyanide of potassium, after previous acidulation with acetic acid, and, finally, in being very strongly precipitated by alcohol, tannin, and acetate of lead. They differ in the following particulars. Parotid saliva exposed to the air, becomes rapidly covered with a film of crystals of carbonate of lime, which is not the case with either of the other secretions. At the temperature of boiling water, parotid saliva does not become turbid, while the other secretions always are rendered at least slightly opaque. Boiled with nitric acid and then treated with ammonia, it does not assume the yellow or orange tint which is developed, under similar circumstances,

by the secretions of the buccal mucous membrane and the submaxillary glands; and farthermore, it is only in parotid saliva that carbonate of potash produces a slight precipitate of carbonate of lime.

We return now to the chemistry of the common saliva, which has been oftener and more thoroughly studied than that from the separate glands. One of the most characteristic of its organic constituents, and one of the most important to the due physiological action of this fluid is that known as ptyalin. Unfortunately, however, the greatest confusion prevails among chemists in their statements of the nature, composition, and reactions of this substance. Upon a careful examination of their modes of obtaining it, it becomes manifest that they have been dealing with different substances, and, consequently, there must be discrepancies in their accounts of the physical and chemical characters of ptyalin. This will be plain from a short review of the various descriptions they have left us of their manipulations and experiments.

Berzelius first separated from saliva a substance to which he gave the name of salivary matter or ptyalin. He first evaporated the saliva to dryness, and then exhausted it with alcohol, thus removing the osmazome, fat, chlorides, and lactates. The solid residue being alkaline, was neutralized with acetic acid, and the acetate removed by fresh alcohol. What remained, being dried, was exhausted by water, which took up this ptyalin, and left behind mucus with earthy sulphates and phosphates. "The solution of this matter in water," says Berzelius, "is a little consistent, and is not troubled by ebullition. After evaporation, the salivary matter remains colorless and transparent. If water is then poured upon this last, it becomes at first white, opaque, and mucous, and then dissolves, making a clear solution, which is not precipitated by tincture of galls, chloride of mercury, subacetate of lead nor the strong acids, characters which distinguish this substance from a great number of other animal matters."

Dr. Golding Bird, in reviewing the characteristics of ptyalin, as described by previous chemists,* comes to the conclusion that

* London Med. Gazette, 1840.

it does not exist as a distinct principle. His reasons for this are, first, the discrepancy in the accounts given of the substance by different observers; secondly, the constant formation of new insoluble matter every time the solution is evaporated, a point noticed by Gmelin, Mitscherlich, and Schultz. This character certainly approximates this substance to the albuminate of soda. Dr. Bird's own experiments exhibit still farther this analogy. He prepared some ptyalin, according to the process of Berzelius, and then exposed it to the action of a *couronne de tasses* of thirty-six pairs. "Coagulation ensued at both electrodes, but most copiously at the negative, where an odor of chlorine was evolved; and by no character whatever could it be distinguished from albumen."

Simon's method of obtaining this substance is analogous, but not entirely similar to Berzelius's. A known weight of saliva was evaporated to dryness; the loss of weight thus indicated the proportion of water. The residue was treated with ether, which extracted the fats. The solid mass remaining was next treated with water, which dissolved out the ptyalin, extractive matter, and salts, leaving behind mucus, albumen, and cells. Evaporated to a small bulk, the fluid gives up its ptyalin as a precipitate on the addition of alcohol. This method alone is a sufficient refutation of Dr. Bird's hypothesis, the heat used in the process being high enough to coagulate all the albumen contained in the saliva.

Lehmann says that it is obtained in greatest purity from the spirit-extract of saliva, after repeated extraction with alcohol and ether. It is combined with potash, soda, and lime, which may be separated from it by carbonic or some stronger acid, after which it dissolves, though with difficulty, in water. When separated by the acids, it falls in amorphous flocculi, which, as already said, are difficult of solution in pure water, but dissolve readily in water to which either an alkali or an acid has been added.

Its reactions, as stated by the latter chemist, sufficiently distinguish it from albumen, while they show it to be intimately related to that substance. *Acetic acid*, added to its alkaline solution, throws down a flocculent precipitate which readily dis-

solves in an excess of the precipitate. Boiled with *chloride of ammonium* or *sulphate of magnesia*, the alkaline solution of ptyalin becomes very turbid. The alkaline solution is precipitated by *tannic acid*, *chloride of mercury*, and basic *acetate of lead*, but not by *alum*, *sulphate of copper*, &c. The acetic acid solution is strongly precipitated by *ferrocyanide of potassium*, and when boiled with *nitric acid*, it yields a yellow color. The resemblance, it will be observed, is much more striking between this substance and albuminose, or the modified albumen of Mialhe, than between it and normal albumen. Both these substances, it may be remarked, are albumen, in a state of change, entering the economy. The physiological analogies between ptyalin and the other digestive ferments will presently be alluded to. When these are all considered, it would appear as if this were the result of the waste of some of the tissues of the glands, probably of the mucous membrane of the ducts and their ramifications, still undergoing the process of metamorphosis, and therefore acting as a ferment.

The *ptyalin** of Dr. Wright must not be confounded with the substance we have just described. The most cursory examination of his experiments suffices to convince us of its distinctness.

The following are the means employed by him for preparing a pure specimen of ptyalin: "First, to pass saliva through ordinary filtering paper, and, after filtration shall have been completed; secondly, to exhaust the residue with sulphuric ether: the ethereal solution contains a fatty acid and *ptyalin*. It is to be allowed to evaporate spontaneously; and, thirdly, the residue left by evaporation is to be placed upon a filter, and acted upon by distilled water, which dissolves the *ptyalin* and leaves the fatty acid. If the aqueous solution be carefully evaporated to dryness, the 'salivary matter' will be obtained in a pure state. *Ptyalin*, as thus prepared, is a yellowish-white, adhesive, and nearly solid matter, neither acid nor alkaline, readily soluble in ether, alcohol, and essential oils, and more sparingly soluble in

* Hereafter, when this substance is alluded to, it will be printed in italics, to distinguish it from the ptyalin of other authors.

water. It alone possesses the characteristic odor of saliva; it is unaffected by galvanism and most of the agents which coagulate albumen; it is abundantly precipitated by subacetate of lead and nitrate of silver; feebly so by acetate and nitrate of lead and tincture of galls, uninfluenced by bichloride of mercury and strong acids; the latter considerably heighten its proper odor and impair its solubility, whilst alkalies render it more soluble, and give it the smell of mucus. Moderate heat and oxygen gas also increase its odor; but intense heat or cold diminishes or entirely destroys it. At a suitable temperature, *ptyalin* may be preserved for any length of time without risk of decomposition. The salivary fluid from which *ptyalin* has been removed by filtration, possesses a sickly mucous smell, decomposes much sooner than ordinary saliva, and in the process of decay invariably evolves ammonia. If this fluid be heated, the mucous smell will be increased until the evaporation shall have been continued nearly to dryness, when a slight salivary odor may be recognized, due to a portion of *ptyalin* being liberated from the mucus with which it was previously in combination."

The other constituents of saliva are—extractive matter, soluble in alcohol and water, precipitable by tannic acid, but not by alum; sulphocyanide of potassium; caproate of potassa;* epithelium and mucous corpuscles; chlorides of sodium, potassium, and calcium; a small amount of phosphates; traces of sulphates, lactates, and carbonates. Lehmann says that the quantity of the latter salts in the fresh secretion must be extremely small, and that the alkaline carbonates, which have been observed, are formed during the process of analysis from the action of the atmospheric air. The formation of carbonate of lime, in this manner, in the parotid secretion of the horse, may be easily seen—very beautiful crystals of this salt being formed.

In the parotid saliva of the dog, the solid residue, according to Jacubowitsch, amounts to 0.47 per cent., in which the organic matter is to the inorganic as 29.8: 70.2; the latter consisting of 44.7 of alkaline chlorides, and 25.5 of carbonate of lime. In

* Probably. It is, according to Lehmann, the potash-salt of a not very volatile acid of the butyric acid group. The crystals under the microscope resembled tufts of margaric acid.

the corresponding fluid of the horse, Lehmann found, as the mean of six analyses, 0.708 per cent. of solid residue, in which the organic was to the inorganic matter as 46.1 : 53.9. The mean amount of ptyalin was 0.140 in Lehmann's experiments.

The presence of sulphocyanogen, in the saliva, was for a long time a subject of quite earnest discussion. At last, the question is settled in favor of those who believe it to be a constant ingredient in this secretion. Whatever may be its physiological value, it is a matter of great importance in a medico-legal point of view, to determine whether it is a normal constituent of saliva; for, in a state of sufficient concentration, it strikes with the sesquichloride of iron the same blood-red tint as meconic acid.

Treviranus was the first to call attention to this reaction. It is unnecessary to go into the history of the discussion upon this point, since the question has been already settled. It will suffice to mention the various modes of proving the presence of sulphocyanogen. Dr. Golding Bird's plan is to acidulate the saliva with nitric acid, mingled with chloride of barium, and then to filter. "No change will occur till the mixture be warmed, when sulphuric acid will be formed at the expense of the sulphocyanogen, and a copious precipitate of sulphate of barytes will be formed." Dr. Percy advises that the residue of carefully dried saliva be exhausted with alcohol, and the solution be subjected, in a test-tube, to the action of nascent hydrogen, which, at the moment of its escape, decomposes the sulphocyanogen, generating sulphuretted hydrogen, which may be recognized by its smell and its action upon lead paper. A piece of pure zinc, with sulphuric acid, is a convenient substance for generating the hydrogen. Still farther, the red precipitate with the persalt of iron may be easily tested. If it is a sulphocyanide, heat will temporarily destroy its color; a reaction which distinguishes it equally from the meconates, formates, and acetates. Another simple and easy method of recognizing the precipitate from a solution containing sulphocyanogen, is to drop a crystal of corrosive sublimate in the red fluid. If the tint be produced by sulphocyanide, the color vanishes; if by any of the acids alluded to, it is unchanged.

There are two modes in which the quantitative determination

of this substance may be made. The alcoholic extract may be dissolved in water; the solution filtered to free it from fat; the filtrate concentrated, treated with sulphuric acid and distilled. The distillate must then be saturated with baryta and filtered, and the filtered fluid evaporated. The residue is to be boiled with fuming nitric acid or aqua regia, and the amount of sulphocyanogen calculated from the sulphate of baryta, which separates. The other method is, to precipitate the same aqueous solution with nitrate of silver, to wash the precipitate well, to treat it with water containing nitric acid, which does not dissolve the chloride of silver; the silver is precipitated from the acid solution by hydrochloric acid, a little chloride of barium is added, the solution is evaporated, a little nitric acid being repeatedly added. We thus, also, obtain sulphate of baryta, from which the sulphocyanogen is to be calculated. It must be borne in mind, however, in all calculations of this kind, that, according to Dr. Wright, this ingredient of the saliva is temporarily augmented by any local stimulation of the glands, by the internal use of prussic acid, the cyanides, and sulphur, especially by the last-named substance.

Kletzinsky* has recently investigated this subject. He tested the saliva by letting it drop from the mouth into a small white porcelain basin, and then added, drop by drop, a normal solution of neutral sesquichloride of iron (1 part of Fe_2Cl_3 to 10 of water), stirring the mixture with a glass rod, till the maximum degree of redress was obtained. The following are his results:—

1. Taking the morning reaction as the normal type, the sulphocyanogen is most abundant after meals, and most deficient in the evening.

2. On fasting, it diminishes most rapidly towards evening, and hardly attains its average quantity in the morning.

3. Its quantity is diminished by alcoholic drinks, and is increased by coffee, pepper, salt, and spices; still more so by mustard, garlic, and radishes.

4. Peruvian balsam always causes an augmentation; and musk, in half-grain doses, produces a very great increase.

* Quoted by Dr. Day, in the British and Foreign Medico-Chirurgical Review for July, 1853.

5. The use of iodine diminishes it.

6. In true ptyalorrhœa, the sulphocyanogen is always very much diminished, or actually disappears; but hydrosulphate of ammonia is present as a product of its decomposition.

7. In almost all chronic exhausting diseases, the sulphocyanogen is diminished, while, during convalescence, it is usually a little above the average.

8. It is relatively deficient in infancy and old age, and in the latter months of pregnancy.

9. In all conditions of excitement, whether psychical or somatic, it is always somewhat increased, till depression begins to supervene. It was very much augmented in a male lunatic addicted to onanism, and in an insane woman with nymphomania.

"The only conclusion," says Dr. Day, "at which we can at present arrive is, that the quantity of sulphocyanogen may, in some measure, be regarded as proportional to the intensity of the vital processes."

After dilution with water, saliva lets fall a flaky precipitate, which is dissolved by boiling, and deposited again on cooling. Saliva freezes at a lower temperature than water. Wright says he has never seen the healthy liquid resist 10° F., though in disease it may remain fluid at 0°.

Saliva has a strong affinity for oxygen, absorbs it readily from the air, and imparts it to other bodies. It has been even said to oxidate gold and silver, when, in minute division, they are triturated with it. The latter metal is undoubtedly affected by it. In manufacturing mercurial ointment, it has long been known that the globules are broken down more readily when the operator spits in the mortar, and the oxidizable metals are always more corroded by this fluid than by pure water. Pure saliva, according to Wright, absorbs, on an average, its own volume of oxygen, though this is liable to variation, from two and a quarter times to one-half the bulk of the secretion. This difference is supposed to be due to the carbonic acid gas contained in the secretion, which varies from one-eighth to one-twelfth in volume, though it is sometimes more abundant. This gas is absorbed in the same ratio, but hydrogen and nitrogen in less proportion.

Exposed to the air at a temperature of 60° F., saliva readily putrefies. Decomposition commences at from the third to the seventh day, the ptyalin generally being the first ingredient to suffer. "Ammonia is usually formed during the process of decay; but, if the saliva have been previously heated to 212° F., it decomposes very slowly, and the product of destruction is generally an acid. The addition of an acid to saliva also assists in its preservation; whilst caustic alkali, which almost immediately causes the evolution of ammonia, promotes rapid decomposition. If saliva be carefully evaporated to dryness, it will retain its odor and properties in an unimpaired state for many months."*

The destructive distillation of this secretion produces, according to the same accurate observer we have so often quoted, carbonate of ammonia, oily matter, acetic and lactic acids, but never the hydrocyanic. The residue consists chiefly of phosphates and chlorides, with a little carbonate.

The *analysis* of saliva has been conducted in different ways by different chemists. Wright's method was as follows:—

"The saliva is to be filtered through moderately coarse filtering-paper. On the filter will remain a solid residuum (1), and a clear liquid (2) will have passed through.

"*Examination of Solid Residuum* (1).—It is to be washed thoroughly on the filter with ether, when a residue (A) will be left, and an ethereal solution (B) will be obtained.

"*Examination of* (A).—Exhaust with cold distilled water; this dissolves the chlorides of sodium and potassium (*a*, *b*), which may be obtained by evaporation. The matter left upon the filter is to be dried, weighed, and then incinerated. The amount of loss thus occasioned indicates the proportion of free albumen (*c*). A little ash remains, from which distilled water extracts carbonate of soda (*d*), and leaves phosphate of lime (*e*).

"*Examination of* (B).—Evaporate carefully to dryness. Wash the residuum on a filter with distilled water, and continue to treat with this menstruum until everything soluble in it is removed. The aqueous solution is next to be evaporated to

* Wright, *op. cit.*

dryness, when a residue of pure *ptyalin* (*f*) will be obtained. The matter left upon the filter is a fatty acid (*g*), which is to be dissolved in sulphuric ether, from which, by evaporation, it may be obtained in a pure form.

"*Examination of Filtered Liquid* (2).—This liquid is affected neither by boiling nor by nitric acid; yet it contains albuminate of soda (*h*), which can only be separated by means of galvanism. To this end, it is advisable to reduce the liquid by very careful evaporation, one-third in volume, and then to introduce the wires of a galvanic battery in action; free soda will collect upon the negative pole, and coagulated albumen upon the positive one. In this manner all the albuminate of soda may be removed without decomposing the chlorides.

"The liquid having been thus treated, is next to be very carefully evaporated to dryness, and the dry residuum exhausted with ether, which dissolves the lactates of potassa and soda (*i*, *j*), and sulphocyanide of potassium (*k*). These salts, having been dried and weighed, are to be dissolved in distilled water, and subacetate of lead is to be added to the solution until it shall cease to afford a precipitate. An insoluble sulphocyanide of lead will be deposited, and a soluble lactate will remain in solution. The former, after having been dried and weighed, will indicate the proportion of sulphocyanide of potassium previously existing in the saliva; and by subtracting this weight from that of the original saline matter, the quantity of lactates will also be determined.

"The residuum from which these salts have been separated is to be treated with alcohol, which will remove the remaining chlorides of sodium and potassium, the weight of which is to be added to that of (*a*, *b*).

"After the extraction of the chlorides, the soda which remains in the form of carbonate, is to be neutralized by acetic acid, and the salt dissolved out by alcohol; by evaporating the alcoholic solution to dryness, and exposing the salt to a red heat, the acetic acid will be destroyed, and the soda (*l*) left.

"The remaining solid matter is to be dried, weighed, and incinerated. The loss by incineration determines the amount of mucus (*m*).

"The saline matter left, is to be boiled in distilled water,

which will generally remove a little sulphate or phosphate of potass or soda—usually a phosphate of soda (*n*).

"The last residuum will be a phosphate of lime; its weight must be added to that of (*e*).

"Silica is mentioned as a constituent of saliva. I have never met with it, though I have occasionally discovered a trace of iron."

Simon's plan differs somewhat from this. He evaporated a known quantity to dryness, and thus determined the water. He then treated the residue with ether to extract the fats; and with water to take up the ptyalin, extractive, and salts. "The insoluble residue that had resisted the action of ether and water, consisted of albumen and mucus. Another portion of the saliva was decanted from its precipitate, evaporated to a small residue, and the ptyalin, with a trace of extractive matter, precipitated by alcohol. When the saliva contains a caseous matter (which I have observed in large quantity in the saliva of the horse), the precipitate of ptyalin and casein produced by the alcohol, must be dissolved in water, and the casein then thrown down by the careful addition of acetic acid. In this case, a portion of the casein precipitated by the alcohol usually remains undissolved by the water. I have detected free acetic acid in the saliva, discharged during salivation. In order to determine its quantity, the saliva must be accurately neutralized by a solution of carbonate of potash of known strength; from the amount of the alkaline solution required, the quantity of acetic acid can be calculated. If, in addition to acetic acid, free lactic acid is likewise present, the residue of the saliva, after evaporation, when dissolved in water, will still indicate an acid reaction, because lactic acid differs from acetic acid in not being volatilized at the ordinary temperature used for evaporating animal fluids. In order to determine the amount of free soda in the saliva, the dried residue must be extracted with alcohol, the free soda (which is left in the residue) must be saturated with acetic acid, the resulting acetate of soda extracted with alcohol, evaporated, and by incineration reduced to carbonate of soda."*

Lehmann's method is also different from Wright's, as will be

* Animal Chemistry.

seen by the following account, which we give in his own words, as translated by Dr. Day :—

"In the first place, the saliva must always be filtered, in order to effect the removal of the epithelial scales; unfortunately, however, the saliva is often so viscid and tenacious, that it undergoes decomposition before passing through the filter; indeed, it generally happens that the small quantity of filtered and perfectly clear fluid begins to become turbid, while the greater portion of the fluid still remains upon the filter. In such cases it is often advisable to dilute the saliva with three or four times its volume of boiling water; and after the mixture has been as thoroughly as possible cooled, and the mucous flocculi for the most part deposited, to filter and proceed with the analysis; but as in this case we are not able to separate the soluble from the insoluble portion, it is best not to attempt the whole analysis, since we should only obtain inaccurate results. We might certainly at once evaporate the viscid fluid, in order to extract the residue with alcohol, ether, and finally with water; but independently of the circumstance that the aqueous extract is also difficult of filtration, substances would be taken up by the alcohol and ether, which do not pertain intrinsically to the saliva, but to the epithelial cells, and to the fat and remains of food sometimes mixed with them.

It is obvious that, if, before submitting the saliva to a chemical analysis, we duly examine its morphological elements with the microscope, we can ascertain whether the insoluble parts of the saliva consist merely of epithelial cells and mucous corpuscles, or whether they also contain fat, vibriones, or molecular granules of an organic nature. In saliva which has been for a long time exposed to the air, in morbid saliva, and especially where it exhibits an acid reaction, such granules are of very frequent occurrence. As substances for the most part in an actual state of change, they do not fall within the domain of an accurate chemical analysis. No one can confound mineral substances, as, for instance, crystals of carbonate of lime, with these molecular granules.

If the saliva has been filtered, no interest attaches to any investigation of the residue left on the filter, at least in so far as

the nature of the saliva is concerned, seeing that true saliva contains only soluble substances.

Wright finds his ptyalin in this residue; he cannot, however, possibly have treated this residue with sufficient water, since, in that case, it could not have contained so large a quantity of matter soluble in water as his numbers indicate.

If carbonate of lime be mixed with this residue insoluble in water, it may be easily extracted by very dilute acetic acid, and its quantity subsequently determined.

In reference to the filtered solution, it is generally of interest to determine volumerically the amount of acid which is saturated by a certain quantity of saliva, in order to form an opinion in regard to the alkalinity of the saliva, or, in other words, regarding the quantity of the weakly-combined alkali. In every case, however, the filtered saliva must be neutralized with acetic acid, and then heated; if this gives rise to a turbidity, the albuminous substance which is precipitated must be collected on a filter, and determined quantitatively. The residue left on the evaporation of the filtered saliva is then to be treated in the same manner as we treat the residue in the case of most of the other animal fluids."*

The method of determining the sulphocyanogen, we have already spoken of.

The following are the results obtained by some of the most distinguished observers.

Berzelius found in 1,000 parts of human saliva—

Water	992.9
Ptyalin	2.9
Mucus	1.4
Extract of flesh with alkaline lactates . .	.9
Chloride of sodium	1.7
Soda	.2

* Lehmann's Physiological Chemistry, vol. ii. p. 22, English edition.

The result obtained by Simon, from his own saliva, was—

Water		991.225
Solid constituents—		
Fat, containing cholesterin	.525	
Ptyalin, with extractive matter	4.375	
Extractive matter and salts	2.450	
Albumen, mucus, and cells	1.400	
	——	8.775
		1,000.

Wright's analysis, in which, it must be remembered, the ptyalin differs from that of Berzelius and Simon, gave—

Water	988.1
Ptyalin	1.8
Fatty acid	.5
Chlorides of sodium and potassium	1.4
Albumen with soda	.9
Phosphate of lime	.6
Albuminate of soda	.8
Lactates of potash and soda	.7
Sulphocyanide of potassium	.9
Soda	.5
Mucus, with *ptyalin*	2.6

The analysis published by Frerichs, and copied by Carpenter, in the last edition of his *Principles of Human Physiology*, from which we quote it, does not precisely correspond with either of the others.

Water		994.10
Solid matter—		
Ptyalin, with a little alcohol extract	1.41	
Mucus and epithelium	2.13	
Fatty matter	.07	
Sulphocyanide of potassium	.10	
Alkaline and earthy chlorides and phosphates	2.19	
Oxide of iron		
	——	5.90
		1,000.00

The analysis of Jacubowitsch is given below. The *soluble organic matter* mentioned in it is what the other chemists call ptyalin.

Water		995.16
Solid constituents—		
Epithelium	1.82	
Soluble organic matter . .	1.34	
Sulphocyanide of potassium .	0.06	
Fixed salts	1.82	
		4.34
Loss		0.50
		1,000.00

In regard to these analyses, Wright says he made about twenty of healthy saliva, and that no two of them *exactly* corresponded. The variation between Frerichs and Wright, is especially manifest in the estimation of the sulphocyanide of potassium. Both of them are beyond Jacubowitsch and Lehmann. The first of these chemists found 0.06 parts of this salt in a thousand of his own saliva, and the second states its variation at 0.046 to 0.089. Frerichs's advance upon the last is but trifling.

In regard to the elimination of substances taken into the system through the medium of this secretion, Lehmann shows that many of them pass off more rapidly by the salivary glands than by the kidneys. Thus, iodide of potassium being taken in the form of pill, iodine may be detected in the saliva in ten minutes, while it requires from half an hour to two hours to detect the same in the kidneys. Bromine, mercury, and other sialagogues, obey the same law. Lehmann, like many of the earlier observers, found mercury in the saliva discharged during mercurial salivation. We shall, however, return to this theme again.

The physiological use of saliva has long been a subject of debate among the learned, and it is doubtful whether it can yet be regarded as fully and satisfactorily ascertained. Dr. Wright, in commencing his investigations in reference to this particular, first endeavored to ascertain its influence upon vegetable and animal life. We have no room even for an abstract of his extremely interesting experiments, and refer our readers who

desire information on this subject, to his papers in the *Lancet* for 1842, and to the *British and Foreign Medical Review* for January, 1847. Suffice it to say, that vegetables were injuriously affected by it, while their seeds escaped, and that animals were destroyed by it when their veins were injected with it. Dogs manifested unequivocal signs of hydrophobia in several instances, and in nearly all perished with symptoms of great disturbance of the nervous system. Jacubowitsch and Lehmann both deny that saliva exerts this deleterious influence over either plants or animals.

Pringle's experiments are not to be neglected by the student who wishes to get an idea of the influence which this fluid exerts over the digestive processes. He beat up, in a mortar, two drachms of fresh meat, the same quantity of bread, with an ounce of water, and so much saliva as he thought necessary for digestion; put the mixture in a closed phial, and set it in a furnace. It remained two days without any visible fermentation, but, on the third, the bread and flesh had risen in the water, a sediment was forming, and bubbles of air continually escaping, this action being accompanied by the vinous smell, common to fermenting liquors. When completed, the fluid had a pure acid taste without any putrid smell, from which, indeed, it had been free during the whole time of the experiment. He thought that healthy saliva was "qualified for retarding putrefaction, preventing immoderate fermentation, acidity, and flatulence in the *primæ viæ*." A subsequent experiment with putrid saliva, showed that this liquid in that state brought on fermentation sooner, made the flesh unusually putrid, but, at last, in consequence of the acid generated, removed the offensive odor.

Leuchs is usually supposed to be the first to discover that saliva had the property of converting starch into sugar, but Dr. Wright has expended much learned research to show that this action upon starch was known long before the announcement of that chemist's experiments in 1831. He quotes Boerhaave, Plenck, Mundius, and a host of others to show that the influence of saliva in producing a saccharine fermentation in farinaceous liquids was well known to the older writers. The favorite drink of the American savages, according to the statements of these

authors, was formed by beating up maize, cassava, or some other amylaceous substance with water, into which were thrown, from time to time, fragments of the same substance, which, having been chewed by the women, were thoroughly saturated with saliva, and so acted as a ferment, inducing the desired degree of saccharine change in the mass. Schwann corroborated Leuchs's statement by his experiments. He found that, when boiled starch was digested for twenty-four hours in saliva, it no longer gave a blue tint on the addition of iodine. On neutralizing, drying, and digesting in alcohol, he obtained sugar, recognized by its taste and its property of fermenting with yeast. The residue, which alcohol did not dissolve, was found to be salivary matter and starch altered to a substance resembling gum, with which iodine did not produce a blue tint.

Wright has investigated this subject with his usual accuracy and candor. He ascertained, as the result of a number of experiments, that the production of sugar from starch is a constant result of the action of saliva upon the latter substance. Fresh saliva seemed to have the most powerful action, though this catalytic or zymotic power remained even after boiling. Hydrogen and nitrogen seemed to diminish the activity of the saliva. Oxygen did not appear to increase it. The addition of either acids or alkalies prevented the development of sugar in the mixed liquids.

The same observer was satisfied that this fluid exerted a digestive influence over meats. He found that, on subjecting the same meat to water and to saliva at the same temperature, fermentation went on rapidly in that portion immersed in the saliva, while in that digested in water there was no perceptible change.

The most conclusive of his experiments, however, in this department of inquiry, are those performed on two dogs of about the same weight, and both in perfect health. Into the stomach of one of these animals, after a fast of twenty hours, were injected eight ounces of lean, raw beef, and the same quantity of bread, beaten to a pulp with ten ounces of water. The gullet was tied and the saliva tested, and found to be alkaline. "*In half an hour its strength of alkalinity was at least doubled;* the *quantity* of the secretion was also much augmented. *The alka-*

line reaction of the saliva gradually increased, till, at the end of three hours, it contained 3.14 *per cent. of alkali.*" The animal being killed by introduction of air into the jugular vein, the food was found unaltered, except by the addition of mucus, and the contents of the stomach had a sour smell. That viscus was deeply reddened, the tint being three or four times deeper than is customary during digestion. On the *second* dog the same experiment was performed, differing only in the substitution of *ten ounces of alkaline saliva* for the ten ounces of water in the preceding experiment. The saliva here, too, at the beginning, was moderately alkaline. "*At the end of half an hour the secretion was scarcely altered, either in* character or quantity. When two hours had elapsed the mouth was very frothy, but the saliva was little changed. At the end of three hours the mouth was still frothy, *and the saliva contained only* .89 *per cent. of alkali.* The animal being killed in the same way, the contents of the stomach were found not particularly acid, nor its mucous membrane more vascular than in healthy digestion. The food was reduced to a perfectly homogeneous pulp.

Dr. Wright's conclusions from his experiments are:—

"1. Saliva has the power of modifying, and, to a certain extent, of digesting vegetable and animal substances.

"2. It has a more powerful action upon vegetable than upon animal matters.

"3. The healthy digestive action of saliva is always attended with the evolution of lactic acid.

"4. Filtration, or boiling, diminishes the digestive powers of saliva, but does not destroy them.

"5. Exposure of the saliva to atmospheric air for a moderate length of time, does not materially weaken its digestive powers, but they are enfeebled in the ratio of the putrescency of the secretion.

"6. Oxygen gas assists the digestive action of saliva, but is not essential to it. Carbonic acid gas impairs this action in a mild degree, and hydrogen and nitrogen gases weaken it very considerably.

"7. Acids or alkalies added to saliva, diminish or destroy its digestive properties.

"8. The presence of saliva in the stomach is essential to healthy digestion.

"9. The digestive action of saliva is not possessed, in any efficient degree, by animal mucus, acids, alkalies, or alkaline salts."

According to the same authority, all stimulation of the stomach by alcohol, spices, or acescent food, is accompanied by a marked increase in the alkalinity of the saliva. When spitting much after a full meal, he never failed to have acidity and pain of the stomach, with corresponding alkalinity of the saliva. A dose of carbonate of soda, neutralizing the gastric acidity, *brought down the saliva to its usual standard of feeble alkalinity in a few minutes, and often in a few seconds.* Acids introduced into the stomach, raw turnips, onions, and other indigestible substances, produced the same effect upon the saliva. The importance of this fluid in digestion is farther shown by the dyspepsia consequent upon its waste. This is undoubtedly one of the sources of that ill-health with which inveterate chewers and smokers are sometimes afflicted. "Frequent attacks of dyspepsia, to which I was once happily a stranger," says Wright, "painfully remind me of the injury I sustained in the course of my investigations. I once spat two hundred and fifty drachms of saliva in one week, and from the nature of my experiments, I was often compelled to spit directly after dinner; in that seven days I lost eleven pounds in weight, and was much weakened and emaciated."

The uses of this fluid in the economy are divided, by the author just quoted, into active and passive; the active being, (1) stimulation of the stomach, (2) aiding digestion by a specific action upon the food, (3) neutralization of undue acidity by supplying a corresponding portion of alkali; and the passive, (1) assisting the sense of taste, (2) favoring the expression of the voice, and (3) clearing the mucous membrane of the mouth.

Cl. Bernard, the distinguished French experimentalist, has investigated recently the action of saliva in digestion, and favors Beaumont's views of the mere mechanical agency of this fluid; opinions, we think, sufficiently controverted by Wright, in the experiments just quoted. M. Bernard, however, has certainly

advanced our knowledge of saliva, as will be seen by a brief review of his statements.

We have already mentioned his discovery of the difference, in physical characters, of the different secretions which make up the common saliva. He also found them to differ in their physiological action, that of the parotid and sublingual being to saturate the food, and that of the submaxillary, by its glutinous consistence, to facilitate deglutition. To confirm this opinion, he made an opening in the œsophagus of a horse, whence he drew the alimentary bolus as it descended, and found that it had increased eleven-fold by the imbibition of saliva. He next tied Steno's duct, and found that the animal required forty-one minutes to masticate what before had demanded but nine minutes; and the mass, when withdrawn, was covered with mucus and a glutinous fluid, the interior being dry and friable, and the whole increased in weight only three and a half times. Water seemed to promote mastication as much as the parotidean saliva, this latter being in proportion to the dryness of the ingested substance.

As to its action upon amylaceous substances, Bernard maintains it to be very gradual, and thinks the time the food remains in the mouth to be too short for it to exert any other than a very partial transforming influence upon it, the change being, he thinks, arrested by the acidity of the gastric juice. He killed a dog, fed on potatoes, and found in his stomach only a trace of sugar, but much unaltered starch. He agrees with Magendie in stating that neither the secretion of the parotid nor that of any other of the glands taken separately, nor yet when mixed with each other, exert any transforming influence upon starch; and therefore assigns the source of the active principle to the small buccal glands. Bernard grants that ptyalin possesses this property, but affirms that it is not peculiar to the salivary secretion, being possessed in an equal degree by many animal fluids, as the water in which buccal mucous membrane had been soaked, the serum of the blood, mucus from the nose during coryza, &c., whence he concludes that the salivary substance does not differ from other nitrogenous substances in a state of change.

We have preferred to give the above brief sketch of Bernard's views, without any interpolations of our own, as he is so prominent an observer, and has so especially directed his attention to the digestive fluids. We proceed now to compare his results with those of other experimentalists of equal ability and industry.

The real question is not whether the ordinary saliva possesses a metamorphic power over starch, for that is universally conceded. The true points at issue are, first: Does saliva, as obtained from the mouth, possess a peculiar power of this kind, above that of any other animal fluid? Secondly: Is this power suspended by the agency of the gastric juice, as Bernard affirms? And, thirdly: Can the buccal mucus alone, or any one of these secretions, the union of which composes the ordinary mixed saliva, produce this effect in a sufficient degree to answer the purposes of digestion?

In reply to the *first* question, we ascertain that boiled starch, mixed with fresh saliva and agitated, immediately loses its viscidity, becoming thin and watery. Tested with iodine, the mixture is not rendered blue, an experiment which establishes the absence of starch. Trommer's test exhibits a copious precipitate of suboxide of copper, precisely as it does in all solutions of glucose.

Now it is well known that other substances possess this power. Liebig has shown that gelatine and albuminous and gelatinous tissues, when moistened and exposed to the atmosphere, acquired, after some time, the property of producing this change. Magendie discovered that infusions of cerebral tissue, heart, lungs, and spleen, possessed the same property; and that the serum of the blood at 104° F., or even at the common temperature of the body, or when boiled starch was thrown into the veins, could produce the same metamorphosis. Bernard, therefore, only repeated these well-known experiments, and has advanced nothing at all conclusive; because a fluid which of itself produces an instantaneous change, cannot, with any sort of fairness, be compared with another which requires time and admixture with atmospheric air to induce the same change. It must also be borne in mind, as Dr. Day has suggested, when speculating upon

the influence of these different animal substances, that starch, when exposed to the air for a length of time, and kept at a high temperature, undergoes spontaneous changes. Even those substances which act most rapidly cannot be compared with saliva, as will be seen at a glance by consulting the following table, embodying the results of a very extensive series of researches made by Bidder and Schmidt, with a view of determining this point.

Substances which were mixed with the solution of starch.	Period when the formation of sugar commenced.
1. Saliva of adult men.	The formation of sugar began instantaneously, but it was only in No. 1 that the whole of the starch was so changed that iodine induced no blue tint; in the other experiments, the complete change was effected in various times, the longest being one hour.
2. Nasal mucus of do.	
3. Saliva of a child aged four months.	
4. Saliva of dogs.	
5. Pancreatic juice of dogs.	
6. Pancreatic tissue of ditto.	
7. Parotid tissue of adult pig.	
8. Pancreatic tissue of ditto.	
9. Gastric juice of dogs which had been rendered neutral by their swallowing the saliva.	
10. Mucus from the urinary bladder of the pig.	30 minutes.
11. Saliva of dog, the parotid secretion being excluded.	20 minutes.
12. Pancreatic tissue of a dog, ten days old.	40 minutes.
13. Tissue of submaxillary gland of adult pig.	1 hour.
14. Hepatic tissue of the same animal.	1 hour and 20 minutes.
15. Muscular coat of bladder of the same animal.	1 hour and 30 minutes.
16. Acid gastric juice of dogs in which there were no epithelial cells from the buccal mucous membrane.	1 hour and 30 minutes.
17. Tissue of submaxillary gland of dog ten days old.	2 hours and 15 minutes.
18. Parotid tissue of the same animal.	3 hours.
19. Mucus from the mouth of a dog whose salivary ducts had been tied a fortnight previously.	After 3 or 4 hours traces of sugar appeared, but the solution of starch remained thick and viscid.
20. Aqueous extract of the detached buccal mucous membrane of the same animal.	
21. Parotid tissue of the same.	
22. Tissue of submaxillary gland of the same.	

Substances which were mixed with the solutions of starch.	Period when the formation of sugar commenced.
23. Parotid secretion of the dog.	Traces of sugar appeared after 8 hours.
24. Submaxillary secretion of ditto.	
25. Orbital gland, secretion of ditto.	No trace after 7 hours.
26. Saliva after the exclusion of the submaxillary secretion.	No sugar after 2 hours.
27. Acid gastric juice of a dog whose submaxillary and parotid ducts had been tied.	No trace of sugar after 15 hours.

"There are two points to be noticed in regard to the second of these experiments: in the first place, the facility with which a little saliva may become mixed with the nasal mucus, in sneezing and similar movements; and, in the second, the circumstance that, in other similar experiments with nasal mucus, the change did not commence until after a quarter of an hour, or even a longer space of time had elapsed."*

Thus, it will be seen that our *first* question must be answered in the affirmative.

The difficulty in regard to the *second* question, arises from the notion of the necessity of alkalinity to the due performance of this peculiar function of the saliva. It can be shown, however, that this is not essential. Jacubowitsch and Frerichs both assert that acid saliva acts as readily on starch as does the alkaline liquid. Lehmann examined this question, by acidifying saliva with acetic, sulphuric, hydrochloric, and nitric acids, and always found that sugar was formed, when boiled starch was subjected to the action of the acid saliva. He came to the conclusion that acids do not impede the action of saliva or starch, but that, whether the secretion be acid or not, it acts with equal energy at equal temperatures.

The question of the action of gastric juice, therefore, so far as regards its mere acid properties, may be considered as settled. Unfortunately, however, there is still much diversity of opinion among eminent chemists, as to its ascertained effects on the metamorphic process. Thus, Jacubowitsch, Frerichs, and Bence Jones, are positive that this process goes on after the admixture of the insalivated morsel with the gastric juice, and Lehmann

* Dr. G. E. Day, in Brit. and For. Med.-Chir. Rev. for July, 1850.

and Carpenter indorse the statement. The balance of evidence and of authority inclines to this side. But, on the other hand, we find facts that seem to contradict it, elicited by observers of the highest eminence, Bidder and Schmidt among them.

The following experiments have been made by Jacubowitsch:—

Pure filtered gastric juice, obtained from a gastric fistula in a dog, having a strong acid reaction, and containing no morphological elements, was neutralized with strongly alkaline, filtered human saliva, and mixed with freshly boiled starch.

Another portion of the same gastric juice was mixed with the same saliva, till its reaction was decidedly acid, and this was also mixed with a fresh decoction of starch.

Both mixtures, after standing for two hours at a temperature of about 100° Fah., plainly indicated the presence of sugar on the application of Trommer's test.

Other experiments were instituted, and the result of the whole of them, as summed up by Jacubowitsch is that the gastric juice does not impede the metamorphic action of saliva on starch. Bidder and Schmidt confirm this statement, as well as that of Lehmann, already quoted, with regard to the acidity of the saliva.

So far, all these distinguished observers are fully agreed, but on a question which seems to be identical, viz. the presence of sugar in the stomach, after a meal of starch has been taken, we find them to differ in their statements.

Bidder and Schmidt found, for example, that when the gastric fluid is alkaline, in consequence of the quantity of saliva which has been swallowed, as happens with animals fed after a long fast, the starch is immediately changed; but when it is strongly acid and contains little or no buccal epithelium, it does not begin to affect a solution of starch in less than an hour and a half, and then only slightly. Here, however, the action of the saliva is not arrested, but only impeded by the extreme dilution. This, and not the acidity, is probably the cause of the delay. These experiments would seem to show that the rapidity of the metamorphosis is directly proportioned to the quantity of saliva present in the stomach.

By another series of experiments, these same observers are led to conclude that sugar is often absent in the stomachs of

animals fed on starch. Hence, Dr. Day remarks, the sugar, which must have been formed in the mouth, has either been immediately converted into lactic acid, and so lost in the gastric juice, or else it has been immediately absorbed. He inclines to the latter opinion, because we have positive proof that the stomachs of neither herbivora nor carnivora possess the property of instantaneously converting sugar into lactic acid. The experiments alluded to were performed by introducing boiled starch into the stomachs of dogs, sheep, and rabbits. In no instance did any conversion into sugar take place.

On the other side, we learn from Frerichs, that, in at least fifty experiments on men, quadrupeds, and birds, sugar was always present in the filtered gastric fluid. Jacubowitsch, by a series of well-devised experiments, seems to have settled the question. He gave boiled starch to a dog which had been kept fasting for twelve hours. Through a previously established gastric fistula he withdrew the contents of the stomach, some four or five hours after the meal, and invariably found that all the starch had been converted into sugar. As a complementary experiment, he tied the parotid and submaxillary ducts of another dog, also laboring under gastric fistula, and fed him on boiled starch. This animal had also been kept fasting for twelve hours. On removing the contents of the stomach, at intervals of about an hour, for nine hours and a half after the meal, he found, on the application of Trommer's test of the microscope and of iodine, that no sugar, nor even dextrine, had been formed. Frequent repetitions of the experiments led to the same results.

The discrepancy between the statements of Bidder and Schmidt and those of Jacubowitsch, is not so great as would at first sight appear. We have not been able to procure their original treatise, and have, therefore, been compelled to rely upon Dr. Day's analysis of it, in his admirable article on the Chemistry of Digestion, already so largely quoted in the present chapter. From that, it would appear that the experiments of Bidder and Schmidt were performed by introducing the starch directly into the stomach, by means of elastic tubes, or through a gastric fistula. Jacubowitsch, on the contrary, fed his dogs

on the boiled starch, so that he effected the natural and intimate admixture of the saliva with the food. Every particle of the starch was thus brought into contact with the ferment, which was transmitted into the stomach along with the bolus. His dogs also had fasted, so that they had abundance of saliva. In the experiments of Bidder and Schmidt, however, this intimate admixture did not take place; the natural stimulus of feeding was not applied to the glands, so that the due amount of saliva was not obtained; the substance was introduced in such a way, that no action whatever could take place except upon the surface; and, finally, the only saliva which could act upon the starch was that which the animals might have swallowed. Now, from the habits of dogs, this could not have been present in any great quantity. From these considerations, it does not appear possible to institute a comparison between these two sets of experiments. The difference of the circumstances attending the different observations, is so great, that Jacubowitsch's deductions cannot be affected by the experiments of his preceptors.

It must also be borne in mind that these results of Bidder and Schmidt have not been confirmed by other observers. Lehmann, experimenting in the same way, obtained totally different results. He always found sugar in the stomach of the animal in ten or fifteen minutes after the bolus of starch had been introduced. Farthermore, Dr. Day, the translator of his work, informs the public that in his third volume, the English translation of which has not yet been published, in reviewing the results obtained by Bidder and Schmidt, he adheres to the opinion he first advanced.

We think, therefore, that a due weighing of the evidence adduced on both sides will compel us to answer the *second* question in the negative.

The *third* question divides itself into two parts. The first part of it, which relates to the action of buccal mucus, has already been answered by the experiment of Jacubowitsch, which has just been detailed. That shows conclusively that the secretion of the buccal mucous membrane possesses not the slightest influence over the metamorphosis of starch, a result confirmed by Bidder and Schmidt in the experiments, No. 19 and 20, which we have given in the above table.

Where, then, does this saccharifying power reside? Mialhe obtained his *salivary diastaste* by precipitating human saliva with absolute alcohol. Ptyalin, mucus, and salts must have been mingled together in this precipitate. The discoverer affirmed that so powerful was the action of this so-called *diastase*, that one part of it readily effects the metamorphosis of 8,000 parts of starch at a temperature of 37°. Lehmann has totally failed to detect such a potent energy, and comes to the conclusion that "the metamorphosing force is neither concentrated in the admixture of substances indicated by Mialhe nor by myself, nor yet in any other part of the extractive matters of the saliva."

Where, then, does this power reside? Magendie and Rayer found that the parotid secretion of the horse exerted no influence upon starch. Marshall and Garrod, however, in experimenting on the fluid derived from a Stenonian fistula in the human subject, found that it could convert starch into sugar. Bernard found that, in dogs, neither the submaxillary nor the parotid secretion possessed any such power. Bidder and Schmidt confirm his statement on this point, but oppose his views in regard to buccal mucus, as we have already seen. They found that the saccharifying power resides in no *one* of these secretions.

Jacubowitsch, after satisfying himself, by the experiments we have already detailed, of the inactivity of the buccal mucus by itself, tied the ducts of a single pair of glands, allowing the secretion of the others to mix with the mucus of the mouth. It mattered not whether the secretion of the submaxillaries or that of the parotids was thus cut off; in either case, starch digested with the dog's saliva was converted into sugar in the course of five minutes. An artificial mixture of either of the secretions with the buccal mucus possessed the same power, but no sugar was produced when starch was digested in a mixture of the submaxillary and the parotid secretions.

Bidder and Schmidt have repeated these experiments, and their results differ somewhat from those of Jacubowitsch. They found, for example, that parotid saliva, when mixed with pure buccal mucus, exerted no very marked influence over the metamorphosis of starch; while a mixture of the submaxillary secretion with the mucus acted as powerfully as common saliva.

Their results, in regard to these points, are summed up by Dr. Day in these words:—

"1. They agree with Bernard in regarding the parotids as *glandes aquipares;* in short, as yielding a secretion which is unquestionably intended to moisten and saturate the dry food, but whose principal object is connected with the general metamorphosis of the fluids within the body, and which is devoid of any marked action on starch.

"2. By the union of the submaxillary secretion and that of the buccal mucous membrane, there is formed that peculiar ferment which almost instantaneously converts starch into sugar. This active principle is not contained in the cells or other solid particles suspended in the saliva, for the filtered fluid exhibits an undiminished force; and, indeed, this property is not destroyed when, by the addition of a little alcohol, we precipitate the mucus, and (entangled in it) these solid particles."

It may be observed here that, in young children and young animals, in whom the secretion of saliva is limited, or altogether absent, this metamorphic action is very feeble. In very young infants there is no secretion of saliva at all. If equal parts of the saliva of an adult and of a child at the breast be mixed with starch, it will be found that while the action *commences* almost instantaneously, it is *completed* in very different times. When the saliva of the adult man is used, the change is over almost immediately, while, when that of the child is mixed with starch, the process occupies a full hour.

According to Lehmann, cane-sugar, gum, bassorin, and cellulose remain unchanged in the saliva; yet, in certain species of sugar, long-continued digestion, at a high temperature, produces lactic and butyric acids. Recent researches show that no other action than comminution and separation of particles is effected by saliva upon albuminous and gelatigenous food.

Kletzinsky has investigated the influence of *sulphocyanide of potassium* upon digestion. He found that, when amylaceous and albuminous bodies were digested with very dilute solutions of this salt, at a temperature of 100° or 110°, no change took place. Sugar was not found, nor was albumen dissolved. Sugar, with which yeast was mixed, did not ferment in the presence of

the sulphocyanide, and healthy saliva exerted the same retarding influence, while that of mercurial ptyalism had no such property. Certain low fungous growths, such as the Oidium aurantiacum, and the Penicilium glaucum, were destroyed by this salt. Children, who suffered with fungous formations in their mouths, were found to secrete saliva in which this salt could hardly be detected. The opinion of this observer is, that the function of the sulphocyanide of potassium is to check too rapid decomposition and the formation of fungous growths within the system.

Liebig thinks that saliva may be designed to convey atmospheric air into the stomach and intestines. Some objection has been made to this opinion, and certain experiments opposed to it have been cited; but, as Lehmann remarks, they "were not conducted with such accuracy as to exclude all access of oxygen, and they cannot therefore be advanced as sufficient evidence against the accuracy of Liebig's view. There are, moreover, as we know, certain processes, as, for instance, the vinous fermentation, in which it requires the greatest exactitude to demonstrate the necessity of a slight access of oxygen. Then, again, the fact that only mixed saliva, that is to say, saliva which has been in contact with atmospheric air, is capable of metamorphosing starch, speaks rather in favor of Liebig's view than against it. Even if the oxygen, which undoubtedly passes into the primæ viæ with the saliva, exerts no effect upon the process of digestion in the stomach, the use of this gas in the intestinal canal may readily be understood, although it cannot be specially demonstrated. We know that gases are present in the intestinal canal, and that these gases are rich in carbonic acid, and often, also, in hydrogen compounds. The formation of the latter, whose passage into the blood would be followed by very injurious results, must necessarily be greatly limited by the presence of free oxygen. According to the laws of the diffusion of gases, the presence of oxygen in the intestines must diminish the withdrawal of oxygen from the blood, and the supply of carbonic acid and hydrogen to that fluid."*

* Physiological Chemistry, ii. 37.

CHAPTER III.

ON THE MORBID CHANGES OF SALIVA.

Dr. Samuel Wright, whose classification will be followed in this chapter, gives the following table of salivary diseases:—*

Deficient saliva.
Redundant saliva (α. Spontaneous; β. Excited).
Fatty saliva.
Sweet saliva.
Albuminous saliva (α. Transparent; β. White).
Bilious saliva.
Bloody saliva.
Acid saliva.
Alkaline saliva (α. Fixed alkali; β. Ammoniacal).
Calcareous saliva.
Saline saliva.
Puriform saliva.
Fetid saliva.
Acrid saliva (α. *Per se;* β. From foreign matters).
Colored saliva.
Frothy saliva.
Urinary saliva.
Gelatinous saliva.
Milky saliva.

DEFICIENT SALIVA.

Saliva may become deficient temporarily from causes purely physiological. This secretion is subject to the same laws which govern all the others. Among these, none is better known than the arrest of the action of glands in consequence of some strong mental emotion. The insane, who live in a perpetual state of emotional excitement, are remarkable for the general torpor of

* Lehmann objects to this as an unchemical classification, but it is valuable as a nosological arrangement, and has therefore been retained.

the secernents. Narcotics and stimulants, which act especially upon the emotional centres, suspend the secretions.

A familiar example of this mode of action upon the salivary glands, is the extreme dryness of the mouth and throat to which the public speaker who makes his maiden harangue is notoriously subject. The rice ordeal among the Hindoos, is another illustration of the same fact. This is commonly employed for the detection of a thief, and is practised in this way: The suspected parties are placed in a ring, the detector being in the centre. A handful of rice is then given to each individual. All are ordered to chew it for a given length of time, and to reject it upon a leaf or clean piece of bark. The different pallets are then examined, and should one of them be unmoistened by saliva, the unfortunate person, from whose mouth it came, is immediately seized as guilty of the crime alleged. This test may occasionally have subserved the ends of justice, particularly if the culprit were thoroughly convinced of the infallibility of the method.

Morbid deficiency of saliva may arise from obstruction of the ducts, from inactivity of the glands, and from disorder of the stomach. Obliteration of the ducts leads to the disease called ranula, which is a distension of a duct by its proper secretion on account of a closure of its natural outlet. This closure may be congenital, or dependent upon tumors pressing upon the ducts, or on calculi closing them. These will be considered in a separate chapter. We shall only say here that the sublingual gland is most subject to them.

A distinction must be made between common and encysted ranula. The contents of the former variety are only saliva as it comes from the glands; those of the latter are albumen, mucus, and some salts, largely diluted with water. Gmelin states it to be water 94.6, solid matter, 5.4. The latter consisted of albumen, extractive matter, and the salts of the blood.

Gorup Besanez has analyzed the fluid of ranula with the following result:—

Water	95.029
Traces of fat and chloride of sodium .	1.062
Aqueous extractive matter . . .	0.923
Albuminate of soda	2.986

Under the microscope blood and exudation corpuscles were observed, none of the ordinary characters of saliva appearing.*

Inactivity of the glands is common in old age, but is occasionally found in persons otherwise in full health and vigor. As it is a purely local affection, local stimulants will generally be sufficient entirely to relieve it.

Disease of the stomach, especially obstinate indigestion, is often accompanied by a disagreeable dryness of the mouth dependent upon salivary deficiency. It is usually relieved by tonics, assisted, if necessary, by local stimulants.

REDUNDANT SALIVA.

Redundant saliva may be *spontaneous*, the fluid remaining healthy; or *excited*, the secretion being depraved by an alteration in its constituents or by the presence of foreign matter.

It is present in infants sometimes from birth, sometimes even in the fœtus, but is most common as an accompaniment of dentition. It is not our purpose to go into a regular pathological history of these diseases. We consider them only as they bear upon the chemical history of this fluid, and as throwing light upon the various influences of the secretion on the teeth.

The specific gravity of the saliva in infantile ptyalism is 1003.1 to 1005. It is oftener deficient in ptyalin and in sulphocyanogen than the saliva of adults. Being generally produced in local asthenia, it is liable to an occasional variation in quality, consisting in a predominance of its albuminous constituent. "I have known this," says Dr. Wright, "to equal 3 per cent."†

Drivelling belongs to the other end of life, and is an eminently asthenic disease. It is also found in idiots. Wright says he has seen the specific gravity of the discharged saliva as low as 1001.1; often 1003, and never above 1005. "It is commonly clear and transparent, like water, and seldom has the blue tinge which distinguishes the healthy secretion. It froths very little when agitated, is often deficient in albumen, and contains less ptyalin and sulphocyanogen than natural; the latter I have

* Rees. Article Saliva, in Cyclopædia of Anatomy and Physiology.

† Wright, *op. cit.*

more than once found to be wanting, though the usual saline constituents were present in their accustomed quantity. The secretion is sometimes alkaline, but oftener neutral."

Vogel has examined the saliva of spontaneous salivation, and gives this table:—

Water	991.2
Ptyalin, osmazome, fat, and albumen .	4.4
Salts of soda, potash, and lime . .	4.4
	1000.0

Mitscherlich and Guibourt found no increase in the solid constituents, while the sulphocyanogen and ptyalin were deficient.

Though in gastric diseases the saliva is usually diminished, there are affections of the stomach which are accompanied by a great increase in the flow of saliva. Nausea, for example, is always attended by this symptom. So is hunger; so is appetite generally, especially when stimulated by the sight, the smell, or even the thought of a favorite dish. Pyrosis has been usually supposed to arise from a morbidly increased flow of fluid from the gastric glands, but Dr. Wright (*op. cit.*) gives reasons for believing that the flow comes chiefly from the salivary organs.

He derives his arguments, first, from the specific gravity of the fluid, which he quotes from Golding Bird. The average specific gravity of the fluids of gastrorrhœa and pyrosis was 1.0097, and that of saliva 1.0081. The lowest saliva was 1.0043, the highest 1.0155, while the lowest pyrotic fluid was 1.0058, and the highest 1.0209. In the second place, he states that the reaction in pyrosis is that of saliva. He experimented on nineteen specimens in which the reaction was strongly alkaline in eleven, feebly alkaline in three, neutral in three, and acid in two. In every case the state of the saliva corrresponded with that of the ejected fluid. This is strengthened, if we consider and appreciate the difficulty of supposing the stomach, which is engaged regularly in secreting an acid fluid, should suddenly change its action and make an alkaline secretion, and then again, without any apparent reason, return to acid secretion again.

One of Dr. Bird's objections to this theory is derived from the behavior of reagents. Sesquichloride of iron, according to

this observer, did not give the characteristic blood-red tinge with pyrotic fluid, but only an orange more or less deep. In reply to this, Dr. Wright states, that the sesquichloride rarely gives the blood-red color with saliva, unless an alcoholic solution of the dried secretion be used, because the animal matters present cloud the solution and obscure the tint. *Ptyalin*, he regards as characteristic of saliva, and he asserts that he has rarely made an examination of the liquid ejected in pyrosis, without finding a sufficiency of this principle to convince him of the nature and origin of the secretion. He gives the following analyses by Dr. Percy as evidence in favor of his view:—

No. I.

Water	938.4
Solid matter, consisting of mucus, chloride of sodium, free soda, and a trace of the matter upon which depends the peculiar and characteristic odor of saliva	16.6

No. II.

Water	994.1
Ptyalin	a trace.
Matter dissolved by alcohol	1.31
Matter left after treating by ether and alcohol; mucus with a trace of albumen	3.63
Saline matter; chlorides of potassium and sodium, with free alkali or carbonate	2.88
Loss	.08
	1000.00

Dr. George Wilson has published an analysis of the fluid of pyrosis, in which he coincides with Mr. Goodsir, in representing the most remarkable character of it to be the presence of a small cryptogamic plant, *sarcina ventriculi*. The organisms are in the form of square or slightly oblong transparent plates of a pale yellow or brown color, varying in size from the 800th to the 1000th of an inch. They were made up of cells with dissepiments, which pressing against one another became bulged out in the middle, so that the organism resembled a soft bundle bound

with cord crossing four times at right angles and at equal distances. From these peculiarities Mr. Goodsir gave it the name of *sarcina*, a wool-pack. The chemical reactions of the fluid differed from those just quoted from Dr. Wright. It was strongly acid, and found to contain free acetic, hydrochloric, lactic, and carbonic acids.

PTYALISM.

Artificial ptyalism is most commonly produced by the preparations of mercury. The quantity of the liquid discharged under the operation of this agent is extremely variable. Its chemical composition has been variously stated.

Observers are especially divided as to the presence of mercury in this fluid. Bostock, Devergie, and Wright could not detect it by the most delicate tests. Gmelin, however, obtained it by Smithson's method, which is a modification of the galvanic test. A large quantity of saliva was treated with nitric acid and evaporated. The dry matter was digested in nitric acid and dissolved in water, the fat was removed by filtration, and a stream of sulphuretted hydrogen passed through the solution. The precipitate obtained by this process contains sulphuret of mercury; it must be collected, digested in nitro-muriatic acid, evaporated, dissolved in dilute hydrochloric acid, and a bit of goldleaf, enveloped in tinfoil or encircled by fine iron wire, suspended in the fluid. The gold is tarnished if mercury is present. No tinfoil should be used which has not been itself tested for mercury. The tarnish must also be examined; for Taylor has shown, that in the presence of free hydrochloric acid, tin may, by galvanic action, be precipitated upon gold. The foil should, therefore, be made into a cornet and introduced into a reduction tube of narrow caliber. Heat being applied, if the stain be mercurial, a dew of minute metallic globules will collect upon the cool part of the tube. Another mode of examination more simple than this is, to let fall a drop of dilute nitric acid upon the stain. If it be mercurial, it is dissolved; if tin, it is rendered white and opaque from the formation of the oxide of that metal.

Lehmann has always found the metal in the fluid of mercurial

ptyalism, both by dry distillation and by the galvanic test, his little battery being formed of two pairs of very minute plates of copper and zinc, suspended in the acidulous solution. He thinks the cause of failure in Wright, and those who think with him, to be twofold. First, they have often examined the buccal secretion only, since, in the first stage of salivation, this constitutes almost the entire bulk of the sputa, the salivary glands being affected later; and secondly, unless the evaporation be conducted with very great caution, the mercury readily volatilizes with the aqueous vapor.

The specific gravity of the saliva, according to Wright, is increased prior to the occurrence of actual ptyalism. He attributes this augmentation of density to an excess of albumen, rarely of mucus, and regards it as the first indication of the action of mercury upon the salivary glands, preceding fetor and the tumefaction of the gums. The greatest specific gravity he met with in commencing ptyalism, was 1.059. In one case, in which violent salivation set in six hours after a dose of five grains of calomel, it was only 1.0048. After the discharge has fairly commenced, the density of the liquid diminishes, and continues low till the action of the glands begins to diminish. Golding Bird estimates it at 1.0043, Thomson at 1.0038, and Wright has found it as low as 1.0015. When separated from the shreds of mucus, which occasionally troubles it, it is nearly as limpid and thin as water. Generally, as the excitement of the glands decreases, the secretion thickens and contains excess of fatty matter.

The sulphocyanide of potassium is very variable in its proportions, some specimens furnishing not a trace of it, while from others Wright obtained 3 per cent. In the majority of instances he observed an increase of sulphocyanogen.

The quantity of mucus is often unnaturally increased; frequently it is adventitious, being derived from the mucous membrane of the mouth, which becomes detached, and is then partially dissolved in the secretions. "The specific gravity of the fluid is thus considerably heightened, and its transparency disturbed. The epithelium is at first suspended like nebulæ in the mass of fluid, but if left at rest, it gradually subsides as a gray-

ish jelly-like sediment, and leaves the supernatant liquid comparatively clear. At other times the *proper* mucus of the saliva is unusually abundant, but the intermixture is so perfect, that, notwithstanding the increased amount of animal matter, there is no observable turbidity. The secretion is inordinately viscid, does not drop from the mouth of a bottle, but runs in a stream (*en masse*), and is not easily miscible with water. It does not froth more than common when agitated, nor does boiling furnish any extra coagulation. I have more than once, under these circumstances, remarked the entire absence of albumen."* Often, however, the saliva of mercurial ptyalism contains albumen in excess.

It is usually increased in alkalinity, and thoroughly transparent, though sometimes, as already intimated, turbid from the admixture of mucus and epithelium. It froths greatly when agitated, and does not recover its clearness readily by rest. It absorbs oxygen rapidly, decomposes easily, and rarely deposits any sediment till this last change has commenced.

The quantity of *ptyalin* is often increased, whence arises the sharp, penetrating taste and smell for which this morbid saliva is so remarkable. Should pus mingle itself with the liquid, *ptyalin* disappears, and the pungent odor is lost. When *ptyalin* is abundant, the saliva decomposes with unusual rapidity, evolving an excess of ammonia. The reaction is almost constantly alkaline, and Wright makes it an element in prognosis; the change of this fluid from acidity to alkalinity, in febrile and inflammatory affections, being often the first sign of amendment. The exceptions to alkalinity are scrofulous and scorbutic cases, and excessive salivation. In the latter instances, the secretion becomes exceedingly offensive, and loses its characteristic properties. It is usually of a dark brown or fawn color, sometimes intermixed with blood. When first discharged, it is opaque from clouds of mucus and epithelium, which are gradually deposited as a bulky sediment, and the supernatant liquor is left clear, and of a brownish or reddish color. "The secretion seldom contains *ptyalin*, and is often also deficient in sulphocyanogen. It

* Wright, *op. cit.*

readily decomposes, and then becomes additionally offensive, and very ammoniacal. Its odor appears to depend upon a fatty matter which is separable by ether and by distillation. This saliva bears little resemblance to the natural secretion, except in being furnished by its glands. It exerts no digestive action upon starch, and is very liable to produce nausea or vomiting, if swallowed."*

L'Heritier gives, as the mean of three analyses of the fluid of mercurial ptyalism:—

Water . . .	970.0	in place of	986.5
Organic matters .	28.6	"	12.6
Inorganic matters .	1.1	"	1.9

The mean amount of ptyalin was 2.6. The increased quantity of organic matters he accounts for by the increased action of the buccal mucous membrane.

Simon† has published an analysis of saliva from a patient who had just concluded a mercurial course of four weeks' duration. It had an acid reaction occasioned by the presence of free acetic acid. It was very viscid, of a yellow color, and possessed a sickly, disagreeable, acid smell. No mercury was found in it. After evaporation to dryness, all the acid reaction had disappeared, showing the absence of lactic acid. It contained a very large quantity of semifluid fat, a considerable amount of albumen, and traces of caseous matter. Many fat vesicles, epithelium cells, and so-called salivary corpuscles, were visible under the microscope. 1000 parts contained:—

Water	974.12
Yellow viscid fat	6.94
Ptyalin with extractive and traces of casein	3.60
Alcohol extract, with salts . .	7.57
Albumen	7.77

"The salts consisted of a large preponderance of the chlorides of sodium and potassium, associated with the lactates of

* Wright, *op. cit.*

† Animal Chemistry, 302.

soda and potash, and with a small quantity of the earthy phosphates. On contrasting this saliva with the normal fluid, we are struck with its large amount of solid constituents, arising not from any increase of the ptyalin, but of the fat, the extractive matters, the albumen, and the salts.

Dr. Wright gives three analyses of this fluid:—

	No. 1.	No. 2.	No. 3.
Water	989.8	988.7	987.4
Ptyalin	1.7	1.9	2.7
Fatty acid	a trace.	.4	.7
Albumen with soda and albuminate of soda . . .	1.5	.6	1.3
Mucus with a trace of *ptyalin*	2.1	3.8	3.5
Lactates, Muriates, Phosphates (Potash, Soda, Lime) . .	1.9	2.4	2.6
Hydrosulphocyanates . .	3.	2.2	1.8
	1000.0	1000.0	1000.0

In the analysis No. 1, the sulphocyanide of potassium was separately estimated and found to be .3 in the thousand parts.

Iodine stands next to mercury as a general sialagogue. The mercurial fetor has been stated by some observers to be present in this form of salivation, while others deny that there is either fetor, sponginess of the gums, or loosening of the teeth. The explanation of this discrepancy will probably be found in the facts recently elicited by M. Melsens's researches. This accurate and careful observer shows that mercury may remain a very long time in the system, in consequence, probably, of its property of forming insoluble compounds with the various organic substances of which the body is composed; and that iodide of potassium is capable of dislodging it, and making it soluble, so that it will again enter the current of the blood, and may, consequently, if set free in sufficient quantity, produce its primary effects of salivation, erythema, &c. Dr. Budd relates a case in which, five months after taking mercury, a patient was violently mercurialized in this way by iodide of potassium.

The tendency of iodine and its compounds to pass off through the salivary secretion, has already been mentioned. Like most other substances, however, it may change the organ of elimination, and may be discharged through the skin, the kidneys, or even by means of the fluid evacuated in consequence of the operation of a seton. Under circumstances like these, its elimination by the salivary glands is of course checked, if not entirely suspended.

Pure iodic salivation differs materially from that produced by mercury. The vascularity of the mucous membrane of the mouth and of the salivary glands may be unchanged, but oftener it is increased, the glands especially becoming tumid and tender. The secretion itself contains an unusual amount of mucus or albumen, the excess of one or other of these elements constituting its chief deviation from the healthy state. The unpleasant taste of iodine is often perceived in the secretion, and weight at the root of the tongue, aching of the jaws, and singing in the ears are complained of. An increased flow of tears and of nasal mucus generally accompanies this form of salivation.

Other halogens, especially chlorine and bromine, have been known to salivate. Ptyalism is one of the effects of arsenic, even when given in medicinal doses. Lead and antimony are said to act in the same manner. The terchloride of gold is an undoubted sialagogue, and some obstetricians even fancy that rubbing the gums with metallic gold facilitates dentition and increases the quantity of the salivary secretion. A host of other substances have been asserted to exert the same action. Among them are found opium, conium, belladonna, nux vomica, digitalis, xanthoxylum, and hydrocyanic and nitric acids. Sulphur increases the quantity of sulphocyanogen, as already stated, and, sometimes after the protracted use of this agent, sulphuretted hydrogen has been liberated by the addition of an acid to the saliva. The action of local sialagogues in increasing the alkalinity of the saliva has been already noticed.

FATTY SALIVA.

In addition to the fatty matter found in healthy saliva, adven-

titious fat is often present in this secretion, which is consequently changed in appearance and properties.

The quantity of fatty saliva secreted is usually less than that of the healthy liquid; it is freer and more abundant in the evening; it has a greasy taste and feel in the mouth; when depraved, it is often very offensive, and is sometimes compared to castor-oil; it imparts a sticky or slimy sensation to the whole mouth, and is with difficulty rejected. In these cases, examined by Wright, from whom this description is copied, the specific gravity was 1.0098, 1.0107, and 1.0113. It is usually frothy on the surface, and the bubbles disappear very slowly. Its color is a dull or yellowish white, of variable intensity, never semi-transparent and bluish like healthy saliva. Its smell is greasy and sickly, never normal. The *ptyalin* and the sulphocyanogen are sometimes altogether wanting. It absorbs oxygen sparingly, and exerts but a feeble action upon starch. It imperfectly converts it into gum, and produces no sugar.

Wright's method of analyzing this variety of morbid saliva was carefully to dry the specimen and exhaust the residue with sulphuric ether. On evaporating the ethereal solution, we have fat, *ptyalin*, and sulphocyanide of potassium. The last two are dissolved by washing in cold water, and pure fatty matter remains, which must be collected, dried, and weighed.

His analysis of what he considered an excellent specimen of fatty saliva is—

Water		987.4
Ptyalin		.7
Adventitious fatty matter and fatty acid		3.9
Albumen with soda, and albuminate of soda		1.5
Sulphocyanide of potassium		a trace.
Mucus		2.4
Lactates, Muriates, Phosphates	Potash, Soda, Lime	1.8
Loss		2.3
		1000.0

This state of the saliva accompanies disorders of the alimentary canal, whether these are primary or consequent upon some other affection. In the saliva of a phthisical patient, Landerer found a great number of small fat-globules aggregated into a viscid mass. These globules exhibited the properties of oleic acid. Wright found it present in phthisis, chlorosis, diabetes, jaundice, smallpox, the dyspepsia of gluttony and of intoxication, and in poisoning by ergot of rye. Should it be persistent, he regards it as pathognomonic of disordered function of the lining membrane of the stomach and bowels.

SWEET SALIVA.

This is a disease which is noticed in most of the larger systematic works on the practice of medicine. It is found in conjunction with a variety of morbid affections. The same state of the system which gives rise to diabetes may produce it, and, indeed, the two affections are often coincident. But it often occurs independently of the urinary disorder, and in subjects in other respects perfectly healthy. Robust, active children and adults are sometimes attacked with it in the early part of the day, particularly if the stomach be empty. It more frequently, however, is found in conjunction with gastro-intestinal irritation, and other forms of depraved digestion and assimilation.

"It is either of a light fawn or a dead white color, with mucous nebulæ; froths easily by agitation, but its bubbles are not permanent, scarcely affords a coagulum by heat, is either acid or neutral to test paper, has a mucous or syrupy smell, which is increased by an elevation of temperature; decomposes readily, and furnishes acetic acid."

"It imparts a sense of sweetness to the tongue; not always agreeable, but, for the most part, mawkish or sickly; sometimes followed by a secondary taste of bitterness, like woody nightshade; and, again, by a sense of astringency. It is very adherent to the tongue and mouth, and its impression is often lasting. On its accession it is merely complained of, but its continuance is often very annoying, and occasionally it nauseates distressingly."

It is analyzed by first filtering, as usual, and after separating the *ptyalin* and fatty acid with ether, as before directed, passing distilled water through the filter to complete exhaustion. The saccharine matter is only partially soluble in water, and part of it is therefore found in the filtrate with the chlorides. The rest must be obtained from the residue by exhaustion with boiling alcohol. The chlorides are decomposed by acetate of silver, the liquid filtered from the chloride of silver, the filtrate carefully evaporated to dryness, and the dry residue weighed. The sugar and acetic acid are then got rid of by incineration, the pure soda left must be weighed, the acetate of soda allowed for, and the sugar estimated by difference. On fermentation with yeast, the aqueous solution yields a notable quantity of alcohol, and on evaporation is reduced to a syrup.

Wright's analysis of sweet saliva is :—

Water	986.9
Ptyalin	.3
Fatty acid	.2
Muco-saccharine matter	5.6
Albumen with soda and albuminate of soda	.4
Mucus with a trace of *ptyalin*	2.6
Sulphocyanide	a trace.
Lactates, Muriates, Phosphates (Potash, Soda, Lime)	1.9
Loss	2.1
	1000.0

The fluid analyzed above was obtained from a diabetic patient in whom a spontaneous ptyalism had temporarily occurred.

ALBUMINOUS SALIVA.

The normal variation in the quantity of albumen in saliva is set down by Wright at .02 per cent. for the minimum, and .5 for the maximum. Any proportion of albumen beyond these limits, either way, constitutes disease.

Albuminous saliva may be classed under two heads, the transparent and opaque varieties. The first of these is almost perfectly transparent, colorless, and untroubled by nebulæ. It has less *ptyalin* and more sulphocyanogen than the healthy secretion, is very tenacious, froths excessively when agitated, and coagulates at 212°. Its specific gravity and alkalinity are great. It decomposes easily, becoming first turbid, then mouldy and ammoniacal. Its action on starch is not so decided as that of healthy saliva. It produces the same quantity of gum, but less sugar and lactic acid.

The opaque variety has a high specific gravity, varying from 1.0168 to 1.0095. It is milky in appearance, absolutely opaque, and when boiled, coagulates in flakes, which subside, leaving a supernatant fluid like whey. There is but a small quantity of ptyalin and sulphocyanide of potassium in this variety of albuminous saliva. It is always strongly alkaline, has a mucous or mouldy smell, froths with permanent bubbles when agitated, absorbs but little oxygen, and has little action on starch. During decomposition, it evolves hydrosulphuret of ammonium, and sometimes hydrocyanic acid. The quantity of albumen varies. In four specimens, Wright found .62, .96, 1.01, and 1.03 per cent. respectively. The salivary glands are always in a disordered or sluggish condition when this albuminous saliva is excreted, and often digestion is more or less seriously impaired. Mercury and iodine, especially the last, produces this disease of the secretion. The drunkard and the glutton are peculiarly liable to it.

BILIOUS SALIVA.

The bile, when once absorbed, or not eliminated by the liver, tinges, as we know, all the fluids and many of the solids of the body. The saliva does not escape the general contamination.

"Bilious saliva chiefly occurs in two forms, colored and colorless; more rarely it is met with containing only cholesterin.

"Colored bilious saliva is of various shades, from a golden yellow to a deep olive. The lighter specimens are generally alkaline, the darker are not uncommonly acid. The specific gravity

of this saliva is greater than natural; its smell is sickly and offensive; its taste bitter and nauseous; it froths easily when agitated, and coagulates abundantly by boiling; protracted ebullition renders it ammoniacal, and deepens its hue; it contains only a minute trace of *ptyalin*, which usually has the color of the original fluid; sulphocyanogen is generally wanting; it exerts scarcely any action upon starch; it readily becomes putrescent, and then evolves either ammonia or its hydrosulphuret."*

Wright has analyzed it, and gives the following as the contents of a single specimen, the only one, apparently, which he examined:—

Water		986.7
Ptyalin		.5
Fatty matter and fatty acid		1.3
Biliary matter		3.2
Cholesterin		.4
Albumen with soda and albuminate of soda		1.9
Mucus		1.6
Carbonates (Potassa)		
Muriates (Soda)		2.3
Phosphates (Lime)		
Loss		2.1
		1000.0

His process of analysis was, first, to remove the ptyalin and fat by ether, then to exhaust the residue with boiling alcohol. By carefully evaporating and crystallizing, he then separated the cholesterin; he then extracted the biliary matter, leaving the chlorides, by digesting absolute alcohol upon the residue of the last process.

"Colorless bilious saliva, as its designation is intended to signify, is free from any appearance of intermixture with biliary matter. Still, it is never so transparent as the natural secretion, and has either a dead white or a slightly dingy aspect. It is

* Wright, *op. cit.*

sometimes bitter, but more frequently imparts a mouldy taste to the tongue. It is always alkaline, with an abundance both of albumen and mucus. Its sulphocyanogen is deficient though rarely wanting; *ptyalin* is present in rather less proportion than natural, and its odor is not recognizable in the saliva, whether cold or hot. The addition of nitric or muriatic acid produces, after a few minutes or a few hours, a dull yellow color, which gradually deepens to a faint olive. Protracted boiling and spontaneous decomposition give rise to the same effect in an inferior degree.

"This saliva will convert a small quantity of starch into gum, but it never generates any sugar.

"Saliva which contains cholesterin free from intermixture with biliary matter, is of rare occurrence. I have seen it only twice—in one instance accompanying dyspepsia with hepatic derangement, and in the other succeeding to an attack of jaundice. In the former case, it lasted for three or four days; in the latter for about a day and a half. The quantity secreted was scarcely more than ordinary, but my attention was directed to it from the patients complaining of a greasy taste in the mouth.

"This saliva is white and shining, and more dense than ordinary; it has an alkaline reaction, does not redden a persalt of iron, and is nearly odorless. Its albumen is in excess, but its saline constituents are in small proportion; it possesses feeble digestive properties, and is slow of decomposition."

BLOODY SALIVA.

This is a rare form of disease and one of no great consequence to the chemist, however important it may be to the practitioner of medicine. Its color depends entirely upon the condition of the hæmatin. It varies from a brilliant red to a deep brown or black. The first variety is darkened by the various gases which similarly affect arterial blood, while the second is not perceptibly brightened by oxygen. Its specific gravity is greater than that of the healthy secretions, its taste bitter, nauseous, saline, or insipid. It is deficient in *ptyalin*, but usually contains the nor-

mal quantity of sulphocyanogen. It is darkened by decay, and during decomposition evolves ammonia. It absorbs oxygen sparingly, and is possessed of but feeble digestive powers.

ACID SALIVA.

The acids with which the saliva is at present known to be contaminated are the acetic, lactic, hydrochloric, oxalic, and uric. It is a matter of great practical importance to ascertain the presence of acid in the saliva, as it exerts so powerful an action over the teeth, corroding them with extreme rapidity.

Acid saliva may have a sour or an exaggerated salivary odor, both of which are increased by heat. It reddens litmus-paper with greater or less intensity. It has about the same specific gravity as the healthy fluid, and sometimes presents an opaque appearance, from the coagulation of its albumen. Its *ptyalin* is in the natural proportion, its mucus and sulphocyanogen commonly in excess.

In analysis, the acetic and hydrochloric acids may be separated from the salts and most of the organic matters, by careful distillation, and then neutralized by an alkali, evaporated and estimated from the salt. Lactic acid is estimated in the ordinary process of analysis. Some of it may be left on the filter. This, with *ptyalin* and fatty acid, is removed by ether. Water separates it with the *ptyalin* from the fatty acid, and the acid is then precipitated from the concentrated aqueous solution by acetate of zinc. Uric acid is left on the filter.

Dr. Wright makes a distinction between the *secretion* and the *excretion* of acid by the salivary glands, attributing the former to some disturbance of the glands themselves or of the digestive apparatus, the latter to some general disorder of the entire system.

"It rarely happens," says he, "that the salivary glands, when in a state of healthy activity, perform an excernent function, to free the blood from any temporary impurity, unless the organ proper for this task shall fail in discharging it. And then, even if the material, oppressive or poisonous to the blood, be capable of being neutralized by any of the constituents of the

saliva, the salivary glands are rather disposed to furnish these constituents in increased quantity to correct the offending matter, than to suffer deterioration or suspension of their characteristic function in becoming partially or entirely emunctories. This rule, however, only applies to the salivary apparatus in a healthy condition; when diseased or disordered, spontaneously or by sympathy, the reverse generally happens."

In corroboration of this opinion, Dr. Wright cites several experiments, which, indeed, appear to be conclusive. He found, on injecting various acids into the veins of healthy dogs, that an immediate and great increase took place in the quantity of the secreted saliva, and that its *alkalinity* was very much augmented. This saliva became acid in one case just before death. In one instance only out of more than twenty experiments, did the salivary glands excrete the injected acid. The subject of this observation was a strong bull-terrier dog, into the veins of which had been thrown three drachms of pyroligneous acid, diluted with six ounces of water. At first, the saliva became very frothy and alkaline, and continued so for six minutes, at the expiration of which time it was discharged very copiously, and found to contain acetic acid. The ptyalism continued for four hours, and it was not until seven hours had elapsed that the saliva had resumed its normal alkalinity.

On the other hand, in diseased or feeble animals, the injected acids were usually discharged through the salivary glands.

Acidity of the saliva may depend upon a spontaneous derangement of the secreting glands. This is usually preceded by the ordinary symptoms of increased vascularity, pain, fulness, tingling, &c. It may be intermittent or continued. Stimulating gargarisms have commonly the effect of restoring the secretion to its normal character of alkalinity. It may also depend upon a general condition of acidity in the system. This accompanies scrofula and other cachexies, and depends upon a variety of circumstances which we cannot at present consider.

Disease of the stomach and bowels is another cause of acid saliva. Donné, who was the first to call attention to this pathological fact, says he never knew a single instance of this derangement in the salivary secretion, in which the functions of the

stomach were healthily performed. This state of the saliva may be absent in some functional disorders of the alimentary canal, but is always present in inflammation of that important tract.

"I have never seen," says Dr. Wright, "a case of gastro-enteritis, whether in a severe or a mild form, in which the saliva was not acid; and I have remarked that one of the first and most favorable indications of recovery is the return of the saliva to a neutral or alkaline state. I have known a patient to suffer for days from an attack of mild gastro-enteritis, and his saliva to be strongly acid, without his consciousness of it, and yet a sudden aggravation of his gastric symptoms to render the saliva almost immediately intolerable from its extreme acidity. On the other hand, I have heard a patient who complained not less of the excoriation and smarting in his mouth than of the burning heat and pain in his stomach, declare the acidity and acid taste of his saliva to be gone in a few minutes after the application of leeches to his epigastrium. The same effect is frequently produced by the counter-irritation of sinapisms and blisters. Nay, I have known the saliva of a gastro-enteritic patient to have a strongly acid reaction before the application of a blister to the epigastrium, and to be equally strong in its alkalinity during the time such blister was in operation.

"The saliva is impregnated with *lactic acid* chiefly in gout, rheumatism, ague, diabetes, and gastro-enteritis; with *acetic acid* in aphthæ, scrofula, scorbutus, smallpox, protracted indigestion, and after the use of acescent wines; with *muriatic acid* in simple gastric derangement from immoderate or improper animal food, and with *uric acid* in gouty affections. When oxalic acid exists in the saliva, its presence will most likely be dependent upon depraved digestion or imperfect assimilation.

"Acidity of the saliva is apt to occur in various other general and local disorders, particularly in fevers, both of the typhoid and inflammatory types; in measles, prior to the eruption, and often subsequently; in miliary fever, when the acidity is sometimes so excessive as to corrode the gums and impart a sensible roughness to the teeth; in maniacal cases, during the exacerbations of which the acid impregnation is often remarkably increased; in phthisis, in protracted venereal disease, in many

skin diseases, in amenorrhœa, rickets, catarrhs, mumps, quinsy, cancer affecting any part of the digestive apparatus, worms, and in the tedious dentition of weakly or scrofulous children."

ALKALINE SALIVA.

This variety, dependent on excess of soda, differs little in external character from healthy saliva. It has a mucous smell, and does not give the red tint with iron, till after neutralization with an acid. It contains excess of albumen, and when the alkali is greatly superabundant, a deficiency of *ptyalin* and sulphocyanogen. It acts less powerfully on starch than the healthy fluid, decomposes readily, and becomes mouldy and ammoniacal.

It is possible that this condition of the saliva may accompany an excess of carbonate of soda administered medicinally. It certainly attends the injection of this salt into the veins. It is remarkable, however, that soda, the alkali peculiar to saliva, is alone eliminated through the salivary secretion, the other alkalies and alkaline earths never being found in it, but always being discharged through the common emunctories. Experiments with mixed carbonate of soda and carbonate of potash were very instructive. The saliva and urine both became alkaline, but the former contained the soda, the latter the potash.

Neuralgia and nervous disturbance generally have a remarkable connection with alkalinity of the saliva. In neuralgia, nervous toothache, and earache, this alkalinity is observable, especially on the affected side. Nervous disorder of the stomach, liver, and other remote organs are also subject to the same law. Epilepsy is also accompanied by alkaline saliva, in some instances, so decided as to impart an unpleasant taste to this liquid. In hysteria, the discharge sometimes amounts to ptyalism; it is of a low specific gravity, limpid, and feebly alkaline. "In the excitement or exacerbation of mania, the saliva is frequently in a state of morbid alkalinity. The secretion itself may be either lavish or limited. I once saw the fury of a madman almost instantly subdued by the sudden occasion of a profuse ptyalism, which continued for nearly three hours. The fluid was very strongly alkaline. In many cases of mania, the saliva is re-

markable for its acidity. Its continued secretion excoriates the lips and gums, and has been known even to corrode the teeth. In such instances, there can be little doubt that the function of the stomach is considerably deranged."*

Ammoniacal saliva is rare. It is dingy and clouded, with a very strong alkaline reaction. The odor is ammoniacal or disagreeably mucous. Fixed alkali, sulphocyanogen, and *ptyalin* are all wanting. It possesses no digestive property. The alkalinity is dissipated by heat, on account of the volatilization of the ammonia. It is secreted in less quantity than usual, and is excessively offensive to the taste. It it difficult to swallow, and clings to the mucous membrane of the mouth.

It indicates a cachectic state of the system. Wright saw it in putrid fever, in scurvy, and in purpura hemorrhagica.

CALCAREOUS SALIVA.

The normal proportion of phosphate of lime is about .6 parts in every 1,000 of saliva. This proportion may be morbidly increased, and then carbonate of lime is also present. Saliva containing this abundance of calcareous matter, deposits it either on the teeth, or in the excretory ducts of the different salivary glands.

This variety of saliva is usually opaque, slightly frothy, and white, like milk. Through the microscope it looks curdy. When the proportion of lime is considerable, the fluid, after standing, deposits a copious precipitate, leaving the supernatant liquid clear. It may be acid, alkaline, or neutral.

In a case of mollities ossium, Dr. Wright found 1.4 per cent. of phosphate of lime in the saliva.

SALINE SALIVA.

The quantity of salts contained in saliva is small but constant, two of them only being subject to variation. These are sulphocyanide of potassium which is liable to diminution, and chloride of sodium, which may be increased.

Excess of this salt in the saliva may depend upon an increase

* Wright, *op. cit.*

of the natural amount present in the blood. Injection of chloride of sodium into the veins of an animal always produces this condition of the salivary secretion. Persons who eat much salt are subject to an increase of this constituent in the saliva. If much liquid is taken, the salt is eliminated through the skin, and in some persons whose cutaneous transpiration is very active, it passes off with great rapidity by this outlet. Men working in salt mines and manufactories are often covered, on the surface of their bodies, and especially their foreheads, with crystals of this salt which has transuded. Dr. Wright says that he once examined the men in a large salt warehouse, and found that those whose skin was impermeable to the saline particles, suffered from a constant salt taste in their mouths, and their saliva was impregnated with chloride of sodium; while those whose skins allowed a ready transit to the salt, were rarely troubled with saline saliva, or with thirst.

It may also be produced by a purely local and idiopathic disorder of the salivary glands. Functional disturbance of the digestive apparatus, too, produces it.

PURIFORM SALIVA.

This is nothing but saliva with an admixture of pus, and is, of course, to be recognized as purulent discharges always are. These need no allusion to them in this place. We shall only say that it has a greater specific gravity and more albumen than normal saliva; that it is always alkaline; seldom deficient in the characteristic elements of the natural secretion; and that it is easy of decomposition, and feeble in its digestive action.

FETID SALIVA.

Various strongly scented substances taken into the system, either at the mouth, or by cutaneous absorption, may be absorbed by the salivary glands, and communicate their peculiar odor to the saliva. The term fetid saliva, however, is not applicable to these conditions of the secretion, but to a morbid alteration of its constitution, which may depend upon either local or general disturbance.

This variety of saliva, according to Wright, is always turbid and flocculent; variable in color, but usually of a red, brown, green, or yellow hue; exhaling a putrid or cheesy odor; greasy and sticky to the touch; deficient in *ptyalin* and sulphocyanogen; either acid or alkaline; having little affinity for oxygen, and scarcely any digestive properties. Its color and smell are due to fatty matter, which is separated by ether or boiling alcohol. Tiedemann and Gmelin suggest, that some phosphorus they found combined with this fat may communicate the unpleasant odor to it. Wright, however, was unable to find uncombined phosphorus in the saliva. It can hardly be necessary to add that this fluid not only does not assist, but, by its nauseous properties, absolutely impedes the function of digestion.

ACRID SALIVA.

No fact is better known than that serious morbid changes may take place without any discoverable alteration, anatomical or chemical, in the solids or fluids of the body. So, too, saliva may be gravely disturbed without any discernible chemical change. The saliva of maniacs is often so acrid as to excoriate those parts of the body with which it comes in contact, and yet analysis reveals the natural constituents in their due proportion. Dr. Wright thinks this saliva capable of communicating hydrophobia. One thing is certain, bites of animals, and even of men, inflicted in fits of furious passion, have produced this terrible malady. If we consider, also, that the most careful examination of hydrophobic saliva has failed to reveal any alteration in the chemical composition of this fluid, we shall have but little difficulty in arriving at the same conclusion with Dr. Wright; that the saliva, thus unnaturally active, differs from the healthy fluid only in possessing, in an extraordinary degree, those properties which are peculiar to it.

Of COLORED SALIVA, it is not necessary to speak at any length. Indigo and some other coloring matters are capable of tinging this fluid. Acetate of lead imparts to it a distinct bluish tint. In the advanced stages of fever, and in purpura, the saliva is often darkly blue. Dr. Wright suspects this to be due to Prus-

sian blue, formed in consequence of the decomposition of the blood.

Frothy Saliva does not differ from the healthy fluid in chemical composition. Its only peculiarities are its appearance, and its undue viscidity. It is pathognomonic of nervous excitement, being found in hydrophobia, epilepsy, &c.

URINARY SALIVA.

Dr. Prout records a case in which, the urine being greatly diminished, ptyalism came on. The saliva had a urinous taste and an alkaline reaction; was opalescent, slightly ropy, and foamed when agitated. Its specific gravity was 1.0055. The soluble salts of lead, mercury, and silver, and the mineral acids produced precipitates in it. Dilute acetic acid caused a precipitate, but none could be obtained afterwards by the addition of ferrocyanide of potassium, showing the absence of albumen. The analysis of Dr. Prout yielded the following results:—

Water	991.35
Animal matter peculiar to saliva	3.33
Alcoholic extract, apparently similar to that obtained from the blood	1.06
Sulphuric acid	.90
Hydrochloric acid	.75
Phosphoric acid	.06
Alkali, partly potash and partly soda . . .	2.55
	1000.00

"The urine of this woman was of an amber color, and slightly opaque. Its specific gravity was 1.0131. It contained crystals of uric acid, and reddened litmus paper more strongly than usual. It contained much less urea than natural, but a large proportion of a brown animal substance, which appeared to render it very prone to decomposition, especially when exposed to heat. With a view of increasing the flow of urine, diuretics were given. These produced the desired effect. The urine was rendered more copious and natural, while the salivary discharge was pro-

portionally diminished." The saliva here was evidently vicarious.

Dr. Wright records a case of granular degeneration of the kidneys, in which, on the suspension of the urinary secretion, vicarious ptyalism set in, to an amount varying from a pint and a half to two pints and a quarter in the twenty-four hours. "The secretion was of a fawn color, viscid, and loaded with films and nebulæ, which finally settled into a heavy, opaque deposit. Its odor, at first putrid, became ammoniacal in a few hours, and the patient complained that its taste was salty and urinous. It was not reddened by a persalt of iron, and it furnished not a trace of *ptyalin*. An alcoholic extract of its dried residue was moderately diluted and treated with nitric acid, when crystals of nitrate of urea were immediately deposited. The proportion of urea never exceeded 5 per cent.; but, until the kidneys resumed their function, neither the salivation was diminished nor was the saliva free from the presence of urea. Directly, however, that the usual reaction was re-established, the action of the salivary glands, and their product, became perfectly healthy."

Dr. Wright also records a case of ascites, arising from subacute peritonitis, in which urea was detected in the saliva. The saliva was of a pale chocolate color, slightly ammoniacal in odor, alkaline in reaction, and disagreeable in taste. The quantity discharged in twenty-four hours was fourteen ounces and a half. No urine was secreted for three days after the ptyalism occurred. From a pint and a half of this saliva, ten grains of urea were obtained by the usual methods.

GELATINOUS SALIVA.

Gelatinous saliva somewhat resembles gum water in appearance; it is imperfectly transparent and somewhat dingy, viscid, and tremulous when cold, but becoming more fluid and clear on the application of heat. It does not easily froth when agitated, decomposes easily and becomes mouldy and sour. Its taste is mawkish, and its smell greasy; its sulphocyanogen and *ptyalin* diminished in quantity, its specific gravity varying from 1.0099 to 1.0101. Its reaction is neutral or faintly acid, absorbs oxy-

gen sparingly, and possesses little or no digestive power. It occurs in a debilitated and depraved state of the system.

Dr. Wright's analysis reveals the following as its constitution:—

Water	987.2
Ptyalin	.6
Fatty acid	.8
Gelatine	3.6
Albumen with soda and albuminate of soda	1.3
Sulphocyanide	a trace.
Mucus	2.5
Lactates, Muriates, Phosphates (Potash, Soda, Lime)	1.7
Loss	2.3
	1000.0

MILKY SALIVA.

This form of saliva is a metastasis from the mammary glands, and may take place either at the commencement of arrest of this secretion, or at its close as a critical flux.

It is an opaque white fluid, sometimes uniform in appearance, but often curdy. Acetic acid increases the coagula. The secretion is healthy, except with the addition of the constituents of milk. Its specific gravity is high, reaching, according to Wright, 1.0125. It is faintly alkaline or neutral, and is easily decomposed. It readily absorbs oxygen, but possesses very feeble digestive properties.

CHANGES OF THE SALIVA IN DISEASE.

We have but little to add to what has already been said upon this subject. We have already noticed the acidity of this fluid in certain inflammatory affections and functional disturbances of the alimentary canal. Another peculiarity of the saliva in inflammatory diseases is a diminution of the normal quantity of water,

as may be seen from the following mean of six analyses made on the saliva in cases of inflammatory fever, pneumonia, and erysipelas. For facility of comparison, the table of healthy saliva constructed by L'Heritier, an average of ten analyses, is placed beside this result:—

	In inflammation.	In health.
Water . . .	968.9	986.5
Organic matter .	30.0	12.6
Inorganic matter .	1.1	.9

The proportion of ptyalin was found to be increased.

In *chlorosis*, saliva suffers from watery degeneration, in the same manner as the animal tissues and secretions generally. In *dropsy* with albuminous urine, the saliva was found by L'Heritier to contain:—

Water	985.9
Organic matter	13.6
Inorganic matter	.5

Scherer has published an analysis of the saliva of a girl of fifteen years of age, who labored under a *scorbutic* disease of the mouth. There was copious ptyalism, the discharge from the mouth amounting to forty ounces in twenty-four hours. The secretion was very liquid, fetid, and alkaline. Its specific gravity was 1004.

The following is the result of the examination of this fluid:—

Water		988.8
Solid constituents—		
A caseous-like substance precipitable by acetic acid	6.5	
Fat taken up by ether	0.6	
Extractive matter and ptyalin	1.8	
Carbonate of soda	1.2	
Chloride of sodium	0.7	
Phosphate of lime	0.4	
	——	11.2
		1000.0

On examination with the microscope immediately after its discharge, the fluid was found to contain a large number of infusoria and confervoid growths.

CHAPTER IV.

MUCUS.

The whole body is inclosed in one vast tegumentary membrane, the internal surface of which differs widely from the external. This internal surface has been called *mucous membrane;* it is covered with epithelium, and kept moist by a secretion constantly flowing over it, which has been called *mucus.* It must be confessed, however, that this term *mucus* has been very irregularly applied, and that many other portions of the body may contain viscid fluids not distinguishable from true mucous juice.

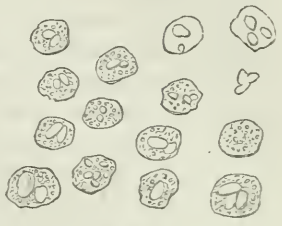
The difficulties of investigation are very great; for, independently of this primary one, the mucous secretion is so small in quantity and so mixed up with other heterogeneous fluids, that it is almost impossible to get at any definite facts in reference to it. It is well known that, during health, the secretion of the mucous membranes is very scanty, and that it is only during disease that any quantity of the so-called mucous secretion accumulates. It would be contrary to all scientific propriety to consider this increased secretion physiological, and to reason from it on the properties of normal mucus. Vogel has found that, under these circumstances, the mucous membranes throw off more corpuscles, and also secrete an albuminous coagulable matter not present in the normal secretion. These circumstances are mentioned to show the difficulty attending the investigation of the chemistry of this secretion.

Fig. 22.

Mucus.

Normal mucus is denser than water, and when not buoyed up by globules of air, sinks gradually in that fluid. When dried, or even when only inspissated, as in some cases of slight irritation of the bronchi giving rise to morning cough, it sinks very rapidly in water. It seems to consist almost entirely of epithelium scales held together by a pellucid juice. These scales vary, of course, in their appearance, with the source whence they are derived.

Fig. 23.



Pus-globules.

Besides epithelium scales, mucus contains globules or corpuscles, which cannot be satisfactorily distinguished from those of pus, either by microscopical or micro-chemical characters. It requires the aid of water or of acetic acid to bring into view the nuclei of the mucus-corpuscles, which then present one or two fissures. In the diseases known as diphtheritic inflammations, *fibrinous coagula*, taking the form of the tube from which they are thrown off, are found, in addition to the elements already enumerated as present in the exudation from these membranes. After these inflammations have subsided, *inflammatory globules* or *granular cells* make their appearance. They are also found in certain inflammations of the mucous membrane which are not diphtheritic. The gray color of such sputa is supposed by Lehmann to depend upon the irregular refraction of light among the numerous highly refracting cells. The usual method of explaining the phenomenon is to attribute it to the soot and fine carbonaceous particles constantly inhaled, more particularly by the inhabitants of large cities, and by certain classes of workmen.

Besides the morphological elements, we find in mucus, *fat-cells*, *molecular* or *elementary granules*, various *cellular formations*, and only occasionally *vibriones* and *microscopical fungoid growths*.

The liquid portion of mucus, according to Simon, invariably exhibits an alkaline reaction. This statement, however, must be taken with allowances. It is always difficult to obtain mucus unmixed with other secretions, so that a source of fallacy is

here introduced which cannot always be guarded against. We have already mentioned that Marshall and Garrod, on investigating this point, in the mucus secreted by the membranes of the mouth in the fœtal state, found the reaction invariably alkaline. Andral, moreover, maintains that perfectly pure mucus is always acid in a normal state. Such an assertion, as Lehmann observes, is not easily proved, since we are unacquainted with any entirely pure mucus. That there are *free acids* in the mucus, every chemist knows. They are included among extractive matters. Nothing, however, is positively known in regard to this free acid, which occurs, among other instances, in the mucus of the mouth, and of the bladder.

When water is added to the clear mucous fluid, a turbidity is visible, which gradually forms itself into a finely granular precipitate. This is the characteristic chemical constituent of mucus, from which it has received the name of *mucin*.

This substance is, however, not invariably insoluble in water, for Scherer has described a mucus soluble in water, and separable from the morphological constituents by filtration. The solution of mucin does not coagulate on the application of heat, but in some instances becomes more fluid, and more like a true solution. Alcohol precipitates it in flakes and threads. Dilute acetic acid precipitates it in viscid flakes, which are sometimes strong enough to admit of traction. This precipitate is insoluble in dilute acetic acid, but, in the concentrated acid, they dissolve with the aid of heat. The mineral acids, in like manner, precipitate the mucin when dilute, and dissolve it again, when concentrated. On the other hand, it dissolves very readily in dilute alkalies, but much less speedily in concentrated solutions. Acetic acid precipitates much less mucin from concentrated than from dilute alkaline solutions, because mucin, if not altogether soluble, forms at least a gelatinous fluid with moderately strong alkaline solutions. In these cases, acetate of potash prevents the mucin from separating perfectly in flakes. Gelatinous mucus is often coagulated by water, so that it loses its translucent, gelatinous character, and becomes denser. Simon supposes that the mucin is held in solution by an alkali, and that the abstraction of this by water causes the change. Ferrocyanide of po-

tassium yields no precipitate with mucin, whether in acid or in alkaline solution, unless albumen or some other protein body be present. Mucus, however, which is *boiled* with concentrated acetic acid, forms an exception to this rule, being copiously precipitated by ferrocyanide of potassium. Concentrated nitric acid colors it yellow, and hydrochloric acid, with the aid of heat and atmospheric exposure, turns it blue. Tannic acid or basic acetate of lead gives a copious precipitate with a weak alkaline solution of mucin, while alum, chromic acid, corrosive sublimate, neutral acetate of lead, and other metallic salts, only produce a slight turbidity.

Pyin, described by Güterbock as a constituent of pus, was supposed, by Eichholtz and others, to be identical with mucin; but a comparison of the reactions of pyin found in pure pus, with those of mucin, will show that this opinion is erroneous.

According to Lehmann, most of the elementary analyses of mucus which have been made, afford us scarcely any aid in judging of the composition of mucin, because the epithelium could not be separated from it. Scherer, however, obtained, from what was probably an enlarged *bursa mucosa* between the trachea and the œsophagus, a mucus which he could filter from the structural components of the fluid. He precipitated the mucin from the solution by means of alcohol, and then boiled it repeatedly with alcohol and ether. Thus purified it gave:—

Carbon	52.10
Hydrogen	6.97
Nitrogen	12.82
Oxygen	28.11
	100.00

No sulphur was found in it, but 4.114% of white ash was obtained from it, which contained alkaline carbonates, and a tolerably large quantity of phosphate of lime.

We subjoin an analysis of normal nasal mucus by Berzelius:—

Water	930.7
Mucin	53.3
Alcohol-extract and alkaline lactates	3.0
Chlorides of sodium and potassium	5.6
Water-extract, with traces of albumen and phosphates	3.5
Soda, combined with mucus	3.9
	1000.0

Nasse has made a very elaborate analysis of the pulmonary mucus expectorated in the morning by a healthy man. No. 1 refers to the mucus itself, and No. 2 to the solid residue:—

	No. 1.		No. 2.
Water	955.520		
Solid constituents	44.480		
Mucin, with a little albumen		23.754	53.405
Water-extract		8.006	18.000
Alcohol-extract		1.810	4.070
Fat		2.887	6.490
Chloride of sodium		5.825	13.095
Sulphate of soda		0.400	0.880
Carbonate of soda		0.198	0.465
Phosphate of soda		0.080	0.180
Phosphate of potash, with traces of iron		0.974	2.190
Carbonate of potash		0.291	0.655
Silica and sulphate of potash		0.255	0.570
	1000.00	44.480	100.000

Jacubowitsch has published the following analysis of buccal mucus:—

Water		990.02
Solid matters :—		
Organic matter soluble in alcohol	1.67	
" " insoluble "	2.18	
Fixed salts	6.13	9.98
		1000.00

The aqueous and alcoholic extracts of mucus have not been very carefully examined. Their quantity is no doubt increased by the secretions of the glands, which are imbedded in the mucous membrane. From this secretion, the true mucus must be carefully distinguished. The intestinal juice, already described, must not be confounded with mucus. It is a glandular product.

In commenting upon the various analyses of mucus, Lehmann observes :—

" Unfortunately, no attention has been paid, in these analyses of the normal mucus, to the relation existing between the potash and the soda. Yet the establishment of this relation is not devoid of importance in the solution of the question, whether the blood-corpuscles take part in the preparation of the mucus as they do in that of most other secretions; or whether the mucus is formed solely from the constituents of the blood-plasma? I know of only one analysis of the kind suited to throw light on the subject, and this yielded more potash and less soda in the ash of the mucus than in that of the blood-serum; but as this mucus had been secreted during an acute catarrh, and besides being very rich in young cells (mucus-corpuscles), contained also some granular cells, it does not afford any conclusive evidence."

In inflammation, or catarrhal inflammation of mucous surfaces, the mucus secreted contains a varying quantity of albumen. Normal mucus may also contain albumen. This is always the case in the mucus of the stomach, which is intermixed with the gastric juice. Tilanus always found albumen, together with the mucin, in the synovia within the joints. This fluid, if viewed anatomically, must be regarded as serous, because secreted by what anatomists term serous membrane. In a chemical point

of view, it must be considered a mucous secretion because mucin, the characteristic ingredient of mucus, is contained in it.

Simon publishes an analysis of morbid nasal mucus which used to accumulate, in thick yellow lumps, in the upper part of the nose of a man aged thirty years. It contained an unusual number of epithelium cells, and a few mucous corpuscles, connected by a pretty thick membrane of coagulated mucin. It contained:—

Water	880.0	
Solid constituents . . .	120.0	
Fat, containing cholesterin . .		6.0
Caseous matter, with pyin or mucin in solution		13.2
Extractive matters, with lactates and chloride of sodium . .		12.0
Albumen, cells, and coagulated mucin		84.0
	1000.0	

From the resemblance of mucin to the protein compounds, we may infer that, on decomposition, it would undergo the same metamorphosis and generate the same acids, and consequently exert the same influence over the teeth as these bodies do while undergoing putrefaction. How an excess of normal mucus might affect these organs, it is of course impossible to determine, so long as we are ignorant of the nature of the free acid which it contains.

The *analysis* of mucus is rendered difficult by the impossibility, in many cases, of separating the solution of *mucin* from the cells which accompany it. When it is not soluble in water, it can only be estimated by filtering it after treating it with dilute ammonia. Unfortunately, however, the swollen epithelial cells obstruct the filtration. Should the filtration be successful, the mucin is thrown down from the neutral or feebly acid solution with alcohol, and from the alkaline solution by dilute acetic acid. The precipitate must be washed with hot spirit, dried at 248°, and washed again with hot water. The rinsings must be collected, and immediately evaporated with the spirituous solu-

tion filtered off from the mucin, and the residue must be extracted with ether, alcohol, and water.

The presence of *albumen* increases the difficulties. "If the mucin," says Lehmann, "were insoluble in water, which appears never to be altogether the case, the separation of the soluble albumen from the insoluble mucin might be very easily effected; but this is by no means the case; for the swollen, gelatinous, or apparently coagulated mucin only gives up the albumen to the water with difficulty and after a long time. Hence, it is necessary, if we desire to obtain a comparatively successful result, to distribute the mucus repeatedly in water, and after suffering it to form a deposit, to pour only the clear fluid upon the filter, repeating the process till the filtered fluid no longer exhibits any opalescence on heating; for the insoluble mucous residue cannot be collected on the filter until the albumen has been completely removed. The quantity of the latter may be determined by the ordinary rules, and a farther separation of the mucin from the epithelium may then be effected by means of diluted alkalies."

If *pyin* also be present, the albumen must first be separated by boiling, and its quantity determined, after which the pyin may be thrown down by acetic acid.

Of the *quantity* of mucus secreted by the membranes in a state of health, it is impossible to form any idea. Valentin believed it to be exceedingly small, or even nothing at all in the normal condition. It can never be obtained from living, healthy animals, in sufficient quantities for analysis, but must be scraped from the mucous membrane of animals immediately after death.

Lehmann believes that the formation of mucus is not limited to a definite spot or associated with any definite tissue. "The conversion of Wharton's gelatine into a substance perfectly similar to mucus in respect to its physical and chemical properties, the gradual transition of the colloid mass of many cysts into perfect mucus, and its occurrence in many exudations proceeding from serous membranes, are facts which cannot be lost sight of in our consideration of the origin of mucus. Tilanus has drawn special attention to the circumstance that epithelial structures are always present wherever there is true mucus. This observation might lead to the assumption that the formation of mucus

is connected with the development of certain cells; that is to say, that its production occurs simultaneously with the development of certain morphological elements. Two views here present themselves for our consideration; one of which is that the albuminates of the liquor sanguinis become decomposed, under certain hitherto unknown conditions, into the substratum of the epithelial cells and into mucus, whereas the latter substance might, in some respects, be considered as a secondary product of this cell-formation, so that the mucous juice in the mucus would hold the same relation to the epithelial cells as the spirituous fluid does to the yeast cells in a mixture which has undergone fermentation. The other view, which seems to be supported by numerous observations made by Scherer and Virchow, refers the origin of the mucus to a partial disintegration of the epithelial cells. All who have followed Frerichs in his observations on the metamorphosis of the cells within the gastric juice, or who have examined them by the microscope in the preparation of artificial gastric juice, will easily comprehend the gradual solution of the gastric cells, and their conversion into a mucous fluid. Such a conversion of cells into a mucous substance would, therefore, at all events, not be without analogy. Scherer and Virchow, however, go still farther, and advance the opinion, based upon several pathologico-histological observations and chemical experiments, that certain colloid substances, and others adapted for the formation of urine, may be converted into mucus under conditions which still remain to be explained, and even without any cell formation; and, hence, they regard the latter mode of development as associated with the existence of colloid or cartilaginous substances. This view is supported not only by the absence of epithelial structures in many mucus-containing cysts, but more especially by the frequently noticed conversion of the gelatine of Wharton into perfect mucus. It appears to us still to require accurate chemical experiments, to decide which of these two hypotheses merits the preference. The elementary analyses which were made by Scherer on a single variety of mucous juice, unfortunately do not enable us to decide the question, both because the atomic weight could not be determined, and because we are still entirely deficient in an accurate analysis

of the epithelial cells, the colloid substance, &c. It remains for us to hope that the investigating powers of men like Scherer may, before long, enrich science with the knowledge necessary for elucidating a subject which is so intimately associated with the advancement of physiology."*

The uses of mucus are to act as a protecting medium to the parts which it covers.

CHAPTER V.

SALIVARY CALCULI.

We have deferred the consideration of these concretions till after treating of mucus; for, though they are chiefly formed from saliva, yet the mucus of the mouth furnishes no inconsiderable portion of their bulk. A distinction must, however, be made in these concretions. It has been customary among dentists to consider all the crusts forming upon the teeth as salivary calculus. In accordance with this universal custom, we shall treat of these concretions, commonly called *tartar*, under this head. The true salivary calculus, however, according to medical parlance, is another thing altogether. It includes only the concretions which occasionally block up the salivary ducts.

These true salivary concretions fortunately are not common in man, but are of frequent occurrence in the ass and horse. They consist chiefly of earthy carbonates mixed with phosphates and animal matters. We copy three analyses from Simon, which will give an idea of the constitution of the calculi found in these animals.

	From an ass. Caventou.	From a horse. Lassaigne.	From a horse. Henry.
Carbonate of lime . .	91.6	84	85.62
Carbonate of magnesia .			7.56
Phosphate of lime . .	4.8	3	4.40
Animal matter soluble in water	3.6	9	2.42
Water		3	

* Lehmann, *op. cit.*

Poggiale analyzed a calculus taken from a man. It was hard, round, tuberculated, of a yellow color, and easily pulverized. It contained 94% of phosphate of lime, with mucus and animal matter.

Wurzer analyzed a calculus from the submaxillary gland of a man. It weighed three grains, was oval, of a grayish-white color, and consisted principally of carbonate of lime and earthy phosphates, with traces of iron and manganese.

Von Bibra, of Erlangen, was fortunate enough to meet with eleven of these concretions in one man, a peasant, twenty-two years of age. Their specific gravity varied from 1.437 to 0.933. He examined one of the lighter calculi, and has published his analysis. He found it to consist of a nucleus made up of albumen and mucus, round which the rest of the calculus had been gradually deposited in concentric layers, as is the case with urinary and other calculi. These layers were made up of various salts intermixed with animal matter, as will be seen by the subjoined table:—

Phosphate of lime	38.2
Carbonate of lime	13.3
Phosphate of magnesia	5.1
Fatty matter with traces of soda . . .	3.1
Organic matter	35.0
Water	5.3
	100.0

In comparing these results with those obtained by Caventou, Lassaigne, and Henry, the reader will be struck with the great excess of phosphates in human calculi, as compared with the concretions taken from the lower animals.

Of *tartar*, there have been few analyses, and these have not been very satisfactory. Writers on dentistry make several varieties of this deposit, but chemists have not as yet, as far as the author is aware, analyzed these different varieties. It was the intention of the writer to have made a series of analyses for this volume; but, though he applied early to his dental friends, he failed to secure specimens for the purpose.

According to Berzelius, tartar contains:—

Phosphates of lime and magnesia	79.0
Salivary (?) mucus	12.5
Ptyalin	1.0
Animal matter soluble in hydrochloric acid	7.5
	100.0

Vauquelin and Laugier have published the following analysis:—

Phosphate of lime, with a little magnesia	66
Carbonate of lime	9
Salivary mucus (including ptyalin?)	13
Animal matter soluble in hydrochloric acid	5
Water and loss	7
	100

Still farther to elucidate this subject, the analyses of Pepys and Dr. Dwinelle, of Cazenovia, New York, copied from Dr. Harris's work on dental surgery, are subjoined:—

	Pepys.	Dwinelle.
Phosphate of lime	35	60
Carbonate of lime		14
Fibrin, or cartilage (?)	9	
Animal matter and mucus		16
Animal fat, or oil	3	
Water and loss	3	10
	50	100

For the sake of comparison, and to elucidate the probable source of this deposit, an analysis by Wurzer of a concretion formed in one of the tonsils is appended. It was of a grayish-white color, marked with rose-red spots, and verrucose; internally it presented no appearance of lamellæ, although it contained an oval nucleus.

Phosphate of lime	63.8
Carbonate of lime	16.7
Animal matter	13.3
Ptyalin with chlorides of sodium and potassium	7.1
Iron and traces of manganese . . .	.1

The presence of ptyalin in the above compound leaves no doubt that saliva assisted at least in its formation, and the close resemblance between it and tartar would seem to imply an identity of origin. Jourdain's notion of a specific glandular apparatus for the secretion of this substance must be given up, since his tartar glands have been proved to be salivary glands, and since there is so strong a resemblance between tartar and true salivary concretions. The mucus of the mouth undoubtedly enters into the composition of this concretion, so that we find it to be only a deposit from the fluids of the mouth upon the teeth, varying of course as the fluids vary, and being soft or hard, as it contains more or less animal matter.

BOOK IV.

CHEMISTRY AND METALLURGY OF THE METALS AND EARTHS USED BY THE DENTIST.

PART I.

THE METALS.

CHAPTER I.

THE VARIOUS METHODS OF APPLYING HEAT, FURNACES, AND AUXILIARY APPARATUS.

The chemist and the metallurgist find it very necessary to be acquainted with that branch of science known as pyronomics, especially with its practical results. Few agents are more powerful than heat in producing chemical changes, whether of composition or of decomposition. It possesses the power of superseding common affinities; or, to speak more philosophically, at different degrees of heat, the chemical affinities of bodies are found to differ greatly.

Thus, when nitric acid and copper are brought together at the ordinary temperature of the atmosphere, a blue, deliquescent nitrate of copper is formed; but if the acid be cast upon red-hot copper, or if the salt just mentioned be heated to redness, the amorphous black oxide of the metal is formed. So, too, if charcoal be mixed with a metallic oxide at common temperatures, no change takes place; but, if a strong heat be applied, the carbon combines with the oxygen of the oxide, carbonic acid is evolved, and the pure metal remains behind. In the latter

example, we find a total difference in the affinities of charcoal and oxygen at different temperatures. The metallurgist constantly takes advantage of this peculiar power of increments of heat in modifying the composition of bodies. By means of this property, he deprives the metals at one time of sulphur or arsenic, at another of oxygen; varying his manipulations with the necessities of the case.

Heat is also used to modify the physical state of bodies. Water is a familiar example of this property of heat. This substance occurs in three different conditions, which are determined by the degree of heat to which it is subjected. At 32° F. and below it, water is solid ice; between 32° and 212°, it is a liquid; at 212° it is a gas or vapor. Any other body may also be made to assume these three conditions, if the necessary increments or decrements can be obtained. Thus, we can volatilize metals, converting them into vapor by a high heat; or, on the other hand, we can freeze gases to solids by exposing them to intense cold. We may, therefore, infer that all bodies are capable of assuming these three forms; and that, in those cases in which we cannot exhibit them thus modified, the cause of our failure is to be found, not in the bodies themselves, but in our limited control over the powers of nature. Were our means of raising or depressing temperature sufficiently great, we might hope to exhibit hydrogen as a solid, or iridium as a gas.

The point that the practical metallurgist desires to obtain is far below these extremes of the powers of cold and heat. He wishes, sometimes, to fuse the metals on which he is working, since he can control them more readily in a liquid state, sometimes only to soften without melting them, as when iron needs to be welded. For this purpose, he needs some knowledge of the higher degrees of heat, as metals are of very different fusibility. Mercury, for example, is fluid at a far lower temperature than that at which water is converted into ice, and iridium has resisted all the most intense heats which the chemist knows how to apply.

So various are the fusing points of the metals, that very different kinds of apparatus are employed for their treatment. Those which come under our observation are not very numerous, and will therefore be treated of somewhat in detail.

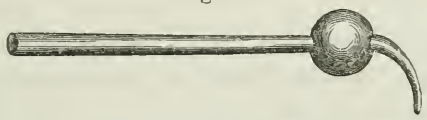
THE BLOWPIPE.

For the minor operations in which heat is employed, the blowpipe is the most common as well as the most useful instrument. The simplest form of this implement is that which is used by jewellers, gas-fitters, and others. It is a simple tube of brass, or other metal, tapering gradually to one end, at which it is curved. This extremity contains a very fine orifice, which is sometimes protected by a raised margin.

Fig. 24.

The fine point of the blowpipe is held against the side of the flame of a lamp, and a steady blast of air from the mouth urged through it. The heat is very highly increased by this method, for reasons which we shall presently specify when we come to give an account of the flame. When the time during which the blowpipe is to be used is short, this form of it answers every purpose. When, however, the instrument is required to be longer used, the moisture from the lungs accumulates in the tube, produces irregularities in the blast, and spirts upon the substance operated on, to the great annoyance of the workman.

Fig. 25.

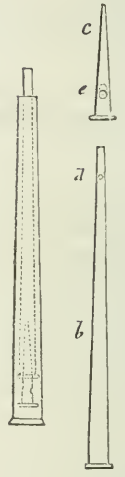


The common method of obviating this will be understood by a reference to the above figure. It consists in appending a globular chamber to the pipe, so that the moisture may collect in it and escape the direct influence of the blast. It was Cronstedt who first introduced this improvement, and it certainly does obviate the difficulty to a very considerable extent. But it does not wholly get rid of the annoyance; for, if the blowpipe is at all inclined, during a protracted operation, the water runs from the bulb and chokes the pipe again.

Wollaston contrived a blowpipe, which is very ingenious and portable, but which is liable to the same objections as the com-

Fig. 26.

Fig. 27.



mon instrument, in containing no chamber to collect the moisture of the breath. It is composed of three pieces, *a*, *b*, *c*. The small end of *a* fits into the large end of *b*, which is closed at its small end, and perforated in one side by a narrow orifice. The piece *c* is closed at its wider end, and slipped over the top of *b* by means of the opening *e*, which is so graduated that, when it is forced down as far as it will go, the hole *d* in the side of *b* will exactly correspond with the narrow canal of *c*.

Gahn's instrument is that which is commonly preferred by blowpipe manipulators. It is composed of three parts, the chief of which is a chamber, of a cylindrical form, an inch in length and half an inch in transverse diameter. Into the upper end of this

cylinder is screwed a long tube, which tapers from the mouth-piece to the chamber. A shorter piece, narrowing to a fine point, is fitted to the side of the chamber. This piece is tipped at its free end with a conical piece of platinum, which is separate from the

Fig. 28.

pipe, and can be applied or removed at pleasure. It is perforated with an extremely small canal. The reason for preferring platinum is to be found in its infusibility at any heat to which the workman can subject it. This affords great facility for the removal of carbonaceous matters which often clog the bore. Nothing more is necessary than to subject it to a very high heat in the blowpipe flame, and these impurities are burned off. When moisture collects in the instrument, it is removed by disconnecting the parts, blowing through the chamber, and wiping it with a dry cloth.

Fig. 29.

Mitscherlich has improved this blowpipe by rendering it portable. The chamber (Fig. 30) is smaller, and attached permanently to the longer tube, which is made to unscrew in the middle, so that the short tube and its platinum jet can be introduced into *B*, and the upper half, *A*, be screwed on.

The cheapest form of the improved blowpipe is that invented by Dr. Black (Fig. 31). It is made of tinned iron, japanned, and consists of a truncated cone, closed at its lower extremity, near which, at the side, is a brass tube, supplied with many platinum jets.

The best material for constructing a blowpipe is silver. The jets, however, ought not to be made of this metal, because, although they answer very well for a time, yet, after being frequently subjected to high heats, they are apt to become brittle. After silver, tinned iron is to be preferred. The great majority of the blowpipes in common use are made of brass; but this alloy is

Fig. 30.

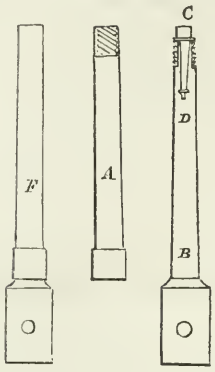


Fig. 31.

objectionable, on account of its easy oxidation and the extremely unpleasant odor and taste which it acquires.

LAMPS.

Any kind of flame may be used for blowpipe operations, provided it be large enough. Engestrom and Bergmann used common candles, but they are objectionable on account of the melting of the tallow on the side towards which the blast is urged, and the frequent necessity for trimming the wick. Spirit-lamps are also used, but they do not give so much heat as oil-lamps, and their only advantage is their cleanliness, which is important when glass tubes are employed, as in certain examinations of volatile substances.

The common form of the dentist's lamp will be seen in Fig. 32. It should hold at least a pint, and have a spout three or four inches long and about three-fourths of an inch in diameter. When spirit is used (and it is preferred by many dentists, among them Dr. Harris), the wick should be large enough to fill the spout pretty tightly. Should this precaution be neglected, the flame, mixed with air, may extend back into the lamp, and an explosion take place.

The best form of lamp for blowpipe manipulations is that invented by Berzelius, a sketch of which is given in Fig. 33.

The movable triangle over the lamp is a supplementary apparatus for the purpose of receiving small crucibles which are to be subjected to the action of the flame. The lamp itself is made of tinned iron or brass. It is 4½ inches long and tapering some-

Fig. 32.

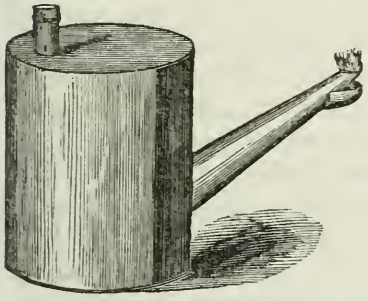
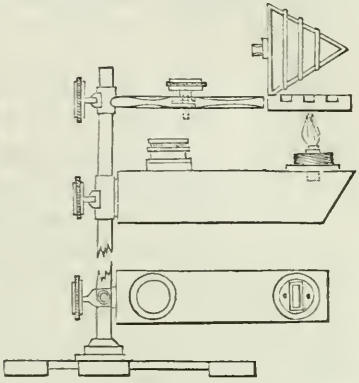


Fig. 33.



what towards the bottom, which is usually narrower than the top. At one end of the upper surface is an opening through which the lamp is filled. This is closed by a screw-cap and a wash-leather. At the other end is a wick-holder, which also may be covered with a screw-cap. The object of these covers is to secure the oil from spilling, and so to render the lamp portable. The front of the lamp is oblique, to permit the ready deflection of the flame. Some of these lamps have a long narrow wick-holder, which is made oblique on its upper surface. The object to be fused is held at the side on which the wick is low, and the blowpipe introduced into the higher end of the flame. This arrangement secures a great body of flame and a corresponding intensity of heat.

The best fuel for this lamp is pure olive oil, or oil of rape. The carbon contained in their flame adds considerably to their heating power. Sometimes a jet of common coal gas is used for the same purpose, but this is inferior to oil in heating power.

Structure of Flame.—A knowledge of the nature and properties of flame being essential to every blowpipe manipulator, we shall give a brief account of it.

The flame of a common candle is a type of all other flames, and has, therefore, been always used as an illustration of flame in general. Flame is nothing but gas or vapor so highly heated that it has become luminous, its brilliancy depending wholly upon its chemical composition. Thus the flame of coal-gas, which contains much carbon, is very white and luminous, whilst that of pure hydrogen is so pale as to be scarcely visible in daylight, or even in the presence of a lighted candle. If we examine closely the flame of a common candle, we find that we can easily separate it into several parts. That portion of the flame which immediately surrounds the wick, represented in the figure by *a*, *b*, is a deep beautiful blue. This portion becomes thinner as it ascends till it gradually disappears. It owes its color to the combustion of carbonic oxide, and is the coolest portion of the flame.

Fig. 34.

The centre of the flame is dark; that is, it is not luminous. It consists of the gases produced by the decomposition of the fat, and is, in the flame we are considering, highly charged with carbon. These gases do not meet, at this point, with sufficient oxygen to burn them, and therefore remain unchanged.* This portion is represented by *c*.

Surrounding this dark spindle-shaped centre, we observe a brilliant white flame *d*. Here the gases combine with the oxygen of the atmosphere. The hydrogen, it is commonly said, burns first, and the intense heat generated by its combustion, ignites the minute particles of carbon which are supposed to be held in suspension by the ascending gas.

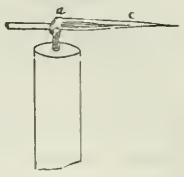
All the gas, however, is not burned in this central spire of flame. A portion of it escapes and burns more slowly, in consequence of its being mixed with steam, carbonic acid, and other products of combustion, together with a little unburnt carbon. This forms the outer dimly luminous envelop *e*, which surrounds

* To prove this, introduce a tube into the central flame, and it will be found that the gas passing through it can be burned at the other end, giving a flame in all respects like that formed around the dark centre.

all flames. The maximum heat is found at the level *f f*, from which it decreases both upwards and downwards.

The blowpipe flame, differing somewhat from the common flame, will now be described. It consists of two distinct parts, one formed immediately before the nozzle of the blowpipe, small, blue, pointed and well-defined, the other yellowish brown and vague.

Fig. 35.



The former is the *reducing*, the latter the *oxidating* flame. These have received their names from the fact that a metallic oxide, introduced into the first flame, is reduced to a *metal*, while, in the second, metals are converted into oxides. The highest heat is just beyond the apex of the blue flame, and it is at the same point that reduction is effected, by means of the unburned carbon therein contained.

Oxidation is very easily effected. All that is necessary is to place the substance at or a little beyond the extremity of the outer flame, and to accommodate the temperature to the metal operated on. A dull red is the best heat for most oxidations. *Reduction* is more difficult, and requires practice and skill to accomplish it satisfactorily. To exercise one's self in it, one of the best plans is to put a small grain of tin on charcoal, and urge the flame upon it. A coat of oxide will show the operator when he has failed to produce a good reducing flame. This is attained by introducing the jet into the body of the flame, so as to produce a small dart, and by using a smaller orifice than is employed for oxidation.

It is not necessary here to speak of *supports* and auxiliary apparatus. The dentist uses charcoal as a support.

The Blast.—To produce a good continuous blast from the blowpipe, necessary as it is to the manipulator, is difficult to the tyro, and requires much practice. Verbal instructions cannot go far towards enabling a student to accomplish this desirable result—it is only to be attained by practice; but a few hints may afford some clue to the beginner who is attempting to acquire this art.

"The practice," says Faraday, "necessary, in the first place, is that of making the mouth replace the lungs for a short time,

by using no other air for the blowpipe than that contained in it." Mitchell's directions in regard to this matter are so simple and clear that we transcribe them:—

"Let the student first observe, that it is easy, after having closed the lips, to fill the mouth with air and to retain it so, at the same time that respiration may be carried on; and if, while the mouth is in this state, a blowpipe be introduced between the lips, it will be found that the small quantity of air which its jet allows to pass through it, will be amply supplied, for ten or fifteen seconds, by the quantity contained in the mouth; and this being repeated a few times, a ready facility for using the blowpipe, independently of the lungs, will be acquired.

"This step being taken, the next is to combine this process with the ordinary one of propelling air directly from the lungs through the mouth, in such a way that when the action of the lungs is suspended during inspiration, the blast may be continued by the action of the mouth itself, from the air contained within it. The time of fourteen or fifteen seconds, during which the mouth can supply air independently of the lungs, is far more than can be required for one or even many more inspirations, and all that is required to acquire the necessary habit is the power of opening and closing the communication between the mouth and the lungs and between the air and the lungs at pleasure.

"The capability of closing the passages to the nostrils is very readily proved; every one possesses and uses it when he blows from the mouth, and that of closing or opening the mouth to the lungs may be acquired with equal readiness. Applying the same blowpipe to the lips as before, use the air in the mouth to produce a current, and, when it is about half expended, open the lungs to the mouth, so as to replace the air which has passed through the blowpipe; again, cut off the supply, as at first, but continue to send a current through the instrument, and, when the second mouthful of air is nearly gone, renew it, as before, from the lungs.

"To some this may be difficult; but if the preceding instructions be followed and persevered in for a short time, a continuous blast may be kept up from ten minutes to a quarter of an hour, without any other inconvenience than the mere lassitude of the

lips, caused by compressing the mouth-piece of the instrument."*

Self-Acting Blowpipes.— These are nothing but modifications of the blast-lamp. The simplest form of this instrument is the common Russian lamp, so generally used that it must be familiar to most

Fig. 36.

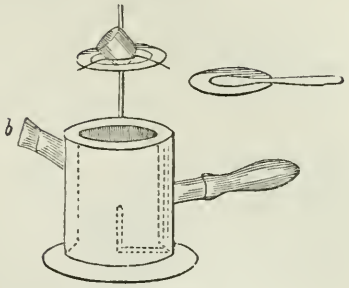
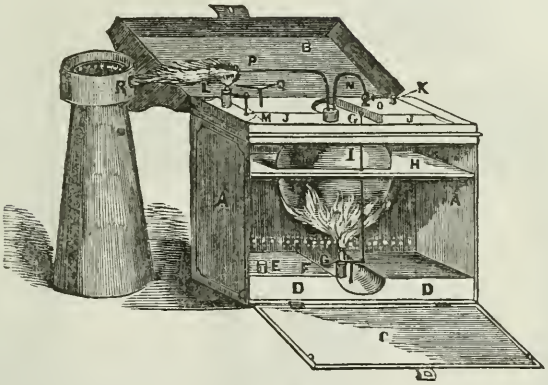


Fig. 37.



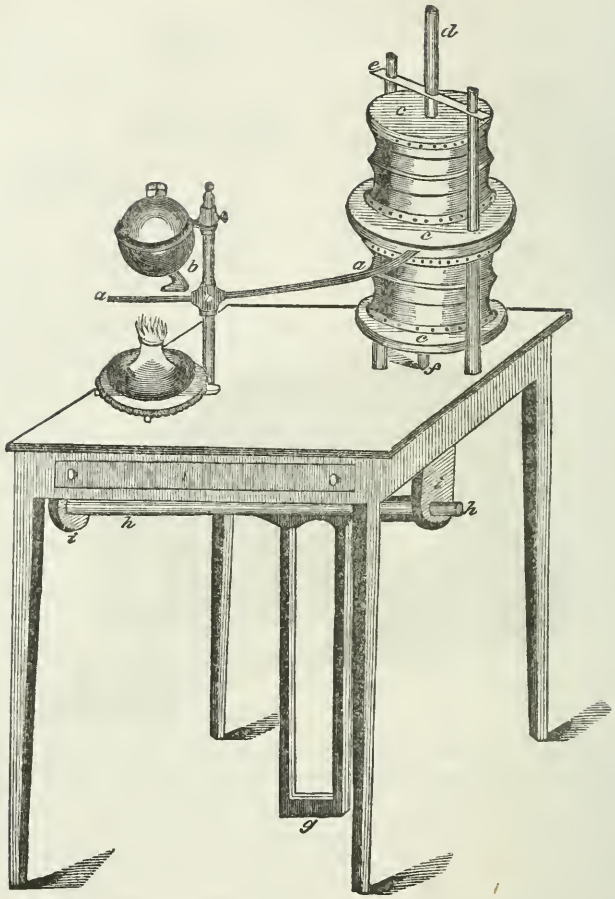
a, a. Side of case. *b.* Top of case thrown back. *c.* Front of case, united by hinge at bottom, and shown in a horizontal position. *d, d.* An oblong fluid vessel for reception of alcohol. *e.* Vent to vessel *d d*, for introduction of fluid. *f.* Burner introduced in groove of vessel *d d*. *g, g.* Movable extinguisher to burner *f*, and not for working the same. *h.* Horizontal plate of tin for sustaining copper globe in place. *i.* Copper globe. *j, j.* An oblong vessel for the reception of alcohol. *k.* Vent to vessel *j j*, for feeding the same with fluid. *l.* Burner, extending from fluid in *j j*. *m.* Extinguisher to burner *l*. *n.* Siphon, extending from fluid in vessel *j j*, to near the bottom of globe *i*. *o.* Stopcock to siphon. *p.* Blowpipe from top of globe *i*. *q.* A small copper trough for retaining condensed vapor that escapes from blowpipe.

The manner of working Dr. Parmly's self-acting blowpipe is very simple. The two vessels, *d d* and *j j*, being filled with alcohol, the stopcock *o* is closed. The mouth is then applied to the end of the blowpipe *p*, and the atmospheric air exhausted from the globe. When the stopcock is turned, the alcohol in vessel *j* will rush through the siphon and fill the globe, should the air continue to be exhausted. For all practical purposes, the globe should be only partially filled, and the stopcock turned so as to close the siphon. The burner *f* should be ignited, and, in about five minutes, alcoholic vapor will be seen to rush out from blowpipe *p*, when the burner *l* should be ignited. The volume of flame can be governed by the extinguishers *g* and *m*.

When the lamp is used for melting metal for castings, the metal should be placed in an iron ladle, and this latter in the furnace previously filled with charcoal, and placed in a proper position, as represented in Fig. 37, for the flame of the lamp to be thrown into it against the coal. When it is desired to melt gold, a crucible should be used instead of the iron ladle.

* Manual of Assaying, p. 109.

Fig. 38.



a, a. Air-pipe leading from the bellows to the lamp. *b.* Vapor-pipe. *c, c, c.* A round bellows, ten inches in diameter. *d.* A rod attached to the upper movable head of the bellows and passing through crosspiece *e*, which serves to keep the head in a horizontal position. *f.* A rod attached in a similar manner to the lower movable head of the bellows, and passing down through the table. *g.* A stirrup attached at the upper end to shaft *h h*. *i, i.* Support for shaft *h h*; by means of an arm projecting backwards from shaft *h h*, and attached to the lower end of rod *f*, the force is communicated from the foot of the artist to the bellows.

readers. It consists of a strong double copper cylinder, from the outer cavity of which a jet pipe passes into the central cylinder. The outer cylinder being filled and the inner half filled with alcohol, the spirit in the latter is set fire. The boiling

alcohol in the outer cylinder is thrown out in a strong jet, which takes fire and produces a very intense heat.

Dr. Jahiel Parmly, of New York, has invented a blowpipe of this kind, of which we give a cut (Fig. 37). A small furnace accompanies it, which is used for heating pieces preparatory to soldering and for fusing metals.

Dr. Elliott, of Montreal, has added to this an improvement (Fig. 38) by which he gets all the benefit of the blast-lamp, together with the advantages of an atmospheric blowpipe. His improvement consists in the introduction of a bellows, the jet of which terminates within the vapor flame. This gives, of course, a true blowpipe flame, having the maximum heat, as usual, at the apex of the blue flame. This lamp is used for soldering, the vapor flame keeping the whole piece redhot, while the tip of the blue dart may be concentrated upon the point at which the greatest heat is needed.

Table Blowpipe.—This is designed for more protracted operations and higher heats than those which have been already

Fig. 39.

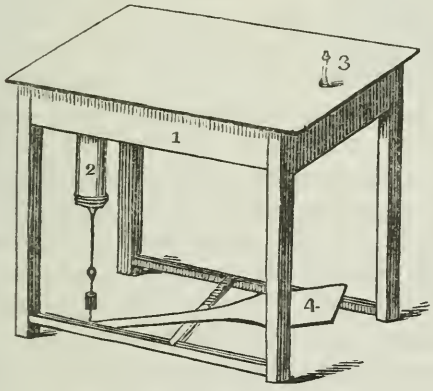
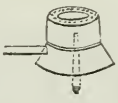


Fig. 40.



alluded to. It consists of a cylinder piston (2), which drives the air into a chamber (1) when worked by the treadle (4). The blast passes through the pipe (3), which may either be attached to a movable jet, or pass into the interior of an Argand burner, as in Fig. 40. This burner is supplied with gas or oil from a movable reservoir. There are several modifications of it, ac-

commodating it both to blowpipe operations and to the portable blast furnace.

FURNACES.

The modifications of furnaces to meet the various necessities of the arts are almost endless. There are, however, a few general principles which govern the builder, and to them it is proposed to call attention in the present section.

The first great division is into *blast*, and *wind*, or *air furnaces*. The latter have received their name from the fact that all the draught in them is obtained by the construction of the chimney, as it is in a common fireplace, while the former are urged by an artificial blast thrown in at the tuyére.

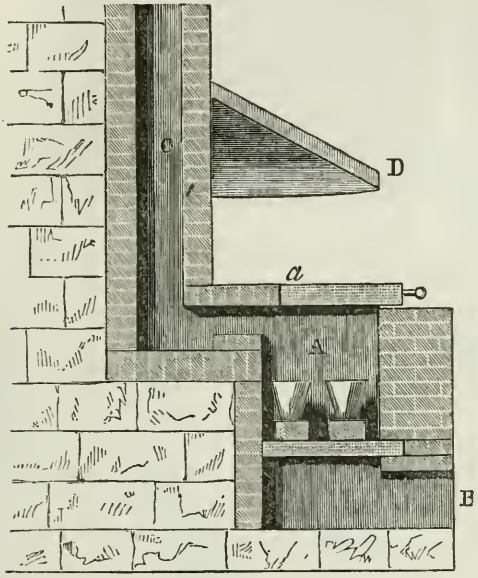
In air furnaces, the heat is applied to the substance to be heated, by bringing it in direct contact with the fuel, as in the *common wind furnace*, or by placing it where the flame will play over it, as in the *reverberatory* or *flame furnace*. (*Flammofen* of the Germans.)

The ordinary construction of a wind furnace is represented in Fig. 41. A is the body of the furnace, which is open at top for the admission of fuel, &c. During working, it is closed by the movable slide *a*, which is made of fire-brick, in one piece, or oftener of a strong iron frame, filled in with brick. In any case, a hole is left in the middle of the slide, provided with a fine clay stopper, which may be removed from time to time, to permit the manipulator to examine the progress of his work. The draft passes through the opening B into the chimney C. The bars of the grate which separate the body of the furnace from the ash-pit *b* are movable, that they may be easily replaced when burned out. Supports, made of fire-brick, rest upon the bars of the grate, and upon these supports the crucibles stand during each operation. All such furnaces should be supplied with a hood D.

The power of such a furnace as this depends entirely upon its dimensions and the height of its chimney. The most economical size is that which will contain four ordinary crucibles. This allows plenty of room for one large operation, or for several small ones conducted at the same time. Fourteen inches square

by twenty-four deep, from the bottom of the cover to the bars, is a convenient size, though for many purposes, such a bulk of fuel as a furnace of this size would consume is unnecessary. The bars should be made of $1\frac{1}{4}$ inch iron, and should be from

Fig. 41.

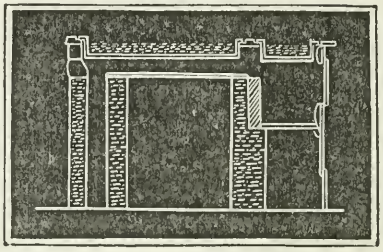


$\frac{1}{2}$ an inch to an inch apart, as the combustibility of the fuel may require. With a chimney 30 feet high, receiving no other flues, such a furnace as this is capable of making an iron assay. A damper is sometimes introduced into the chimney, in order to regulate the draft.

For other purposes, smaller furnaces should be used. The following figure represents the section of one described by Morfit, in his *Chemical and Pharmaceutical Manipulations*. The first part of the flue, passing off from the body of the furnace, is covered in with a sand-bath, and closed below with an iron plate. The flue descends before passing into the chimney, thus leaving between it and the ash-pit a hot-air chamber, in which all the common desiccations may be performed. Another sand-bath closes the furnace itself, instead of the slide already described.

It is useless to point out the advantages and the economy in fuel resulting from such an arrangement as this, to those who have many different operations to perform. For a more minute

Fig. 42.



description, we refer our readers to the work from which we have taken the figure.

The *reverberatory furnace* is rarely used except in large operations. In the small way, a sort of cupola is made by placing a dome over a wind or blast furnace. This differs, however, from the true reverberatory, in the fact that the fuel surrounds the body to be heated, whereas, in that, the entire heat is derived from the flame and its repercussion from the roof.

The *cupelling furnace* has been compared to the *reverberatory* furnace. It is a cupola containing a muffle, in which is placed the material to be heated. This is a semicylindrical oven, made of refractory fire-clay, and closed at one end. On its side are several openings, which allow the passage of a pretty strong draught of air, while they are sufficiently small to protect the assays from accidents arising from the dropping in of cinders. In this muffle the cupels, hereafter to be described, are placed.

Fig. 43.

There are various forms of the cupelling furnace. We give a cut of one described by Morfit, in his *Chemical and Pharmaceutical Manipulations.*

"A A′ is the ash-pan, of diameter sufficient for the reception of the body of the furnace B B′. The door C is for the exit of the cinders and the ingress of the air. The larger opening, D, in the body of the furnace, is for the introduction of the

muffle, and a corresponding one, D, opposite, for a prism-shaped support of baked clay for maintaining the muffle in a horizontal

Fig. 44.

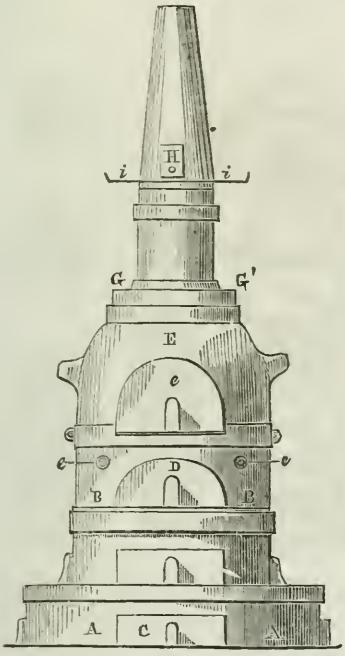
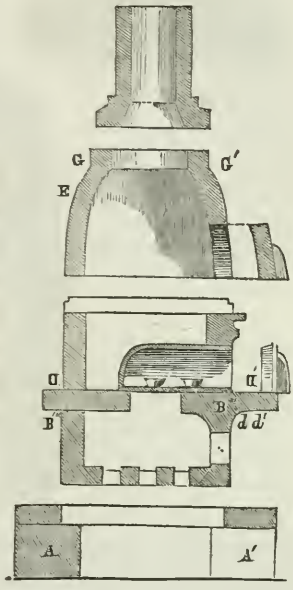


Fig. 45.



position. The mouth-piece, supported by a small platform, affords the facility of admitting or preventing the access of air to the interior of the muffle.

"In the part of the dome E, is a door for the introduction of fuel. The two openings, *e e*, are for the introduction of a poker to arrange the fire.

"At the top of the furnace is a dome G G, to which is adapted a sheet-iron pipe for increasing the draught.

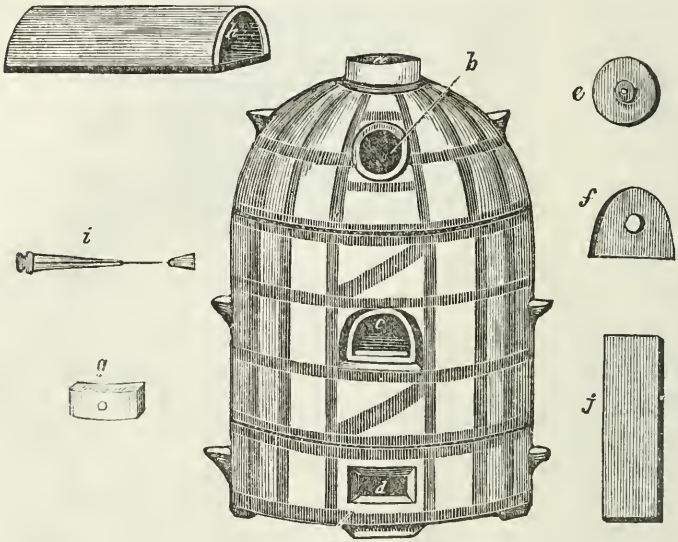
"A sliding door H, and a small circular gallery *i i*, as a support for heated coals, afford additional means of increasing the draught."

The position of the muffle, with the cupola in it, is seen in the section. From this arrangement, it will be perceived it is

equally heated above, below, and at the sides, since the fuel entirely surrounds it.

The common furnace for baking incorruptible artificial teeth

Fig. 46.



A muffle furnace.—*a*. Collar for smoke-pipe. *b*. The opening through which the fuel is introduced. *c*. The muffle-door. *d*. The ash-pit door. *e*. Stopper for the opening *b*. *f*. Stopper for closing the opening to the muffle. *g*. Stopper for the opening to the ash-pit. *h*. Muffle. *i*. Stopper with platina wire and test. *j*. Slide.

is constructed on precisely the same principles as the cupelling furnace. Some modifications, however, are made in the accompanying furniture. Thus, the muffle is fixed, and a slide is provided for the introduction of the paste. The muffle is closed with a door, having in its centre a hole, which is closed by a fire-clay plug. In this is sometimes inserted a platina wire, the extremity of which carries a portion of the paste of which the teeth have been carved. By withdrawing this, from time to time, the progress of the baking can be accurately ascertained.

Blast Furnaces.—The construction of the blast furnace is as various as that of the reverberatory. Many of them are simple cylinders; some are inverted and truncated cones, others double hollow cones applied base to base.

A simple and extremely powerful furnace of this kind, for laboratory use, may be made of two blue-pots, or black-lead crucibles. The larger of these is eighteen inches high, and thirteen in external diameter at the top. Into this a smaller pot, of seven and a half inches external diameter, with its bottom cut away to make an opening of five inches, is introduced. This rests, by its outer edge, on the bottom of the larger pot, the tops of the two being level. The interval between them is filled up with pounded glass pots, to which enough water has been added to moisten the powder. A grate is then dropped into the inner pot, the space below it constituting the air-chamber, that above it the body of the furnace. Finally, a conical hole, one inch and a half in diameter, is cut into the outer pot, opening into the air-chamber. It serves for the introduction of the nozzle of the bellows.

With this simple furnace, not only can pure iron be fused in from 10 to 15 minutes, but rhodium can be melted, and, according to Faraday, platinum run together. All sorts of crucibles are destroyed by it, softening, fusing, and becoming frothy, so that the want of vessels capable of resisting its heat has limited its application.

The opening into which the nozzle of the bellows is introduced is called the tuyére, and is usually so closed with lute as to admit no air between its sides and the blast-pipe. The Messrs. Barron, however, have, within the last two or three years, patented a furnace, which they claim to be a very great improvement. In it the blast passes into a wide tuyére, a considerable space being left between the nozzle of the bellows and the sides of the blast-hole. They think that a greater blast, and consequently a more powerful heat can be obtained in this way than by the ordinary method. The author attempted to use one of these furnaces, as a means of making a more expeditious dry assay of metals. He cannot, however, say that he saw any particular advantage in them. The failure may have been due in part to the bad construction of the furnace, and not to any error in the principle itself. There was no provision for the equal diffusion of the draught, so

Fig. 47.

that the crucible was irregularly heated, and the fire became hollow on one side from the rapidity of the combustion, while on the other it burned very slowly. This, it is not necessary to say, is a fatal defect in a blast furnace for chemical purposes.

CRUCIBLES.

A crucible is a very refractory vessel, in which substances are placed, in order to be raised to a high heat, whether for purposes of fusion or of simple ignition. The materials of which they are made are wrought-iron, platinum, plumbago, clay, and certain admixtures to be presently described.

We shall hereafter speak of those finer varieties of clay, which are used in the manufacture of porcelain. At present, a description of the qualities and composition of refractory clays employed in the manufacture of articles designed to resist high furnace heats, will form a suitable introduction to an account of the properties of crucibles.

When perfectly pure, clay is infusible at the highest heat of a blast, though it may soften and become lustrous, showing that a change resembling fusion is possible. There are, however, very few pure clays. Those from which the workman has to choose his materials, are all contaminated with foreign admixtures, some of which exert a most unfavorable influence over the fusibility of the clay. The most common impurities are oxide of iron, iron pyrites, limestone, graphite, and various organic and bituminous matters.

The greater the number of these ingredients, the more fusible will be the compound. Thus a clay which is mixed with a definite quantity of lime is less fusible than another containing magnesia and lime, though the two earths together weigh no more than the lime alone. The most refractory of the pure clays are those which contain most silica. Rotten-stone, which contains so much silica that it cannot be called a clay, is the most infusible of the aluminous compounds.

It is not, however, only infusibility which is to be considered in the selection of a fire-clay. Many clays, which leave nothing

to desire, as to this point, are nevertheless liable to contract or expand too strongly, so as to split and fly.

It is, therefore, necessary to select a clay more or less mingled with silicious sand, or to introduce some other material, which, without increasing the fusibility of the clay, diminishes this property of too rapid contraction.

According to Wurzer, the composition of the clay and sand of which the Hessian crucibles are made, is as follows :—

	Clay.	Sand.
Silica	10.1	95.6
Alumina	65.4	2.1
Oxides of iron and manganese .	1.2	1.5
Lime	0.3	0.8
Water	23.0	—
	100.0	100.0

An idea of the proper composition of clays for different purposes may be obtained by a comparison of the two following tables. The first is a series of analyses, made by Dr. Richardson, of clays taken from the neighborhood of Newcastle-upon-Tyne, where an extensive trade in fire-bricks and gas-retorts is carried on. The clay for these purposes need not be so fine nor so refractory as that out of which crucibles and glass pots are to be made. These being thinner, require a very refractory material. The second table consists of analyses, by Berthier and Salvetat, of the most celebrated fire-clays employed in the construction of these vessels.

TABLE I.

	1.	2.	3.	4.	5.	6.	7.
Silica	51.10	47.55	48.55	51.11	71.28	83.29	69.25
Alumina	31.35	29.50	30.25	30.40	17.75	8.10	17.90
Oxide of iron . . .	4.63	9.13	4.06	4.91	2.43	1.88	2.97
Lime	1.46	1.34	1.66	1.76		2.99	1.30
Magnesia	1.54	0.71	1.91	trace	2.30		
Water and organic matter	10.47	12.01	10.67	12.29	6.94	3.64	7.58

TABLE II.

Dried at 212°.	Gross Almerode.		Beaufaye, department des Ardennes.	Brierly Hill, near Stourbridge.		Schierdorf, near Passau.
	Berthier.	Salvetat.	Berthier.	Berthier.	Salvetat.	Salvetat.
Silica	46.5	47.50	52.0	63.7	45.25	45.79
Alumina . . .	34.9	34.37	27.0	20.7	28.77	28.10
Oxide of iron . .	3.0	1.24	2.0	4.0	7.72	6.55
Lime	—	0.50	—	—	0.47	2.00
Magnesia . . .	—	1.00	—	—	—	—
Alkalies . . .	—	trace	—	—	—	—
Hygrometric water	—	0.43	—	—	—	0.50
Combined water .	15.2	14.00	19.0	10.3	17.34	16.50

Having thus examined the composition of the clay, the next thing is to examine the quality of the crucibles made from it. It is required in crucibles: First, that they should be able to resist great changes of temperature without breaking; secondly, that they should be infusible; thirdly, that they should not be attacked by the substances fused in them; and, lastly, that they should be impermeable to both liquids and gases. Now, it is impossible to fulfil all these indications, by any material or combination of materials, known as yet to the manufacturers of these vessels. Crucibles are therefore made to fulfil one or more of them, so that the operator can select the variety specially adapted to his wants in any given case.

To furnish a crucible which will bear sudden changes of temperature without breaking, it is necessary, as has already been stated, to mix with the clay certain substances called cements, which are infusible of themselves. Sand, flint, fragments of old crucibles, black-lead, and coke are used for this purpose. The materials selected and the fineness of the powder to which they are reduced, depend entirely upon the purpose for which they are required.

We have already spoken of the refractory character of pure clays free from the metallic oxides and alkaline earths. It has also been stated that they nevertheless soften in a high heat, so that in a wind furnace crucibles made of pure clay soften sufficiently to fall into a shapeless mass. To obviate this, pounded

coke or black-lead is mixed with the clay. This, being absolutely infusible, resists the action of the fire, and furnishes a sort of skeleton to hold up the earthy portions of the vessel. Some judgment is required to mix it properly with the clay, for should the carbonaceous materials be in too gross powder or too large quantity, it will burn out and the crucible will crumble.

The more compact a crucible is, the more will it resist the action of corrosive agents. The materials of which it is composed, and the substances melted in it, will also influence its fusibility. The oxides and fusible silicates attack all crucibles. The alkalies and alkaline earths are sure to destroy clay crucibles. They wear them away layer by layer, till finally the vessels become so thin as to give way to the pressure of the molten mass within them.

Everything else being equal, that crucible will be most impermeable which has fewest pores in it. None of the earthen crucibles are entirely impermeable, unless they have been baked at a heat high enough to glaze them. It is customary to coat these vessels with Willis's lute, which is a mixture of borax and lime, when it is desirable that they should be impermeable.

Composition of Crucibles.—Berthier's analysis of different varieties of crucibles is given in the following table :—

	Silica.	Alumina.	Oxide of iron.	Magnesia.
Hessian crucibles from Gross Almerode	70.9	24.8	3.8	—
French crucibles from Paris	64.6	34.4	1.0	—
" " Beaufoy . . .	72.3	19.5	3.9	—
" " St. Etienne for cast-steel . .	71.0	23.0	4.0	—
English crucibles for cast-steel . . .	65.2	25.0	7.2	—
Glass pots from Nemours	67.4	32.0	0.8	—
" Bohemia	68.0	29.0	2.2	0.5

Examination of Crucibles.—To determine whether a crucible will bear great and sudden changes of temperature without breaking, it is put into a heated furnace, raised to a reddish white heat, and then withdrawn and subjected to the blast of a bellows. If it stand this, it is heated to whiteness, and then plunged into cold water. The best crucibles are unaffected by these tests.

To determine its fusibility, a piece is broken off, taking care that it shall have sharp angles, and then heated to whiteness in a crucible lined with charcoal. If the edges become rounded or translucent, the test-piece is fusible.

The liability to be attacked by metallic oxides is commonly ascertained by fusing litharge in the crucible to be tested. The longer it retains this powerfully corrosive oxide the better it is.

Two crucibles are easily compared as to their permeability, by filling them with water, and ascertaining how long it takes for each of them to become damp on the outside.

Clay Crucibles.—The Hessian crucibles are more frequently used than any others for rough fusions, for which they answer very well. They are, however, very easily attacked by many of the oxides and the alkalies. In a coke-fire they are very liable to fuse, if heated highly and kept too long exposed to the action of the earths and oxides of the fuel. They are accused of being fragile when quickly heated, but I have never had reason to make this complaint of *good* Hessian crucibles.

The London crucibles are very refractory. Beaufaye's French crucibles are still better; they bear changes of temperature well, and resist the corrosive action of the salts and oxides.

Anstey's crucibles are made of two parts of Stourbridge clay and one of the hardest gas-coke. They are heated carefully before the matter to be fused is introduced into them. If not allowed to cool, they will bear from 14 to 18 meltings of cast-iron. Pots made of 8 parts of Stourbridge clay and cement, 5 of coke, and 4 of graphite, have been found to stand 23 meltings of 76 pounds of iron each.

Black-lead crucibles must not be used for fusing salts, as they are permeated by them; nor for metallic oxides, as they reduce them, and are gradually destroyed by them. They are valuable for fusing the pure metals, as they are extremely infusible. They are made of 2 parts of graphite and 1 of fire-clay.

Porcelain crucibles are used for igniting oxides, for fusions of substances requiring a moderate heat, and for sulphuration. The French are better than the Berlin, as they are thinner, and not so apt to crack.

Iron crucibles are used for fusing silicates and a variety of

salts. They should be coated with clay, to preserve them from oxidation.

Silver crucibles are only employed for the fusion of potassa and soda, and the preparation of caustic baryta from the nitrate.

Platinum crucibles are indispensable to the analytical chemist, though not often used by the artisan or the manufacturing metallurgist.

CUPELS.

These are small shallow vessels, flat at the bottom and concave on their upper surface. They are usually made of bone-ash.

The bones are calcined in an open crucible to perfect whiteness. They are then reduced to a powder, which is repeatedly

Fig. 48.

and thoroughly washed in clear water, dried, and sifted. This is now made into a paste with water, in which a very small quantity of carbonate of potash has been dissolved, or with beer. Mitchell uses the latter in the proportion of half a pound to 4 pounds of bone-ash. To make the cupel from this paste, a mould, consisting of a ring and pestle, must be used. The ring is to be filled with the composition; the pestle is then to be introduced, pressed down with the hand, and finally driven home with a mallet. It is then turned lightly round, to smooth the inside of the cupel, and withdrawn. The cupel is removed by tapping gently on its base, dried cautiously on a stove, and then ignited in a muffle, to drive off all moisture.

Fig. 49.

Care must be taken that the powder of which the cupel is made is neither too fine nor too coarse; neither too wet nor too dry. It should be compressed with a certain degree of force. Should the powder be too coarse, and only slightly moistened and compressed, the cupel will be porous, break easily, and

allow the metal to pass through it in small globules. Should it be too fine, too wet, and too strongly compressed, the cupels are too solid, cause much delay, and demand a very high temperature for the completion of the cupellation.

The operation of cupellation will be described under the head of Metallurgy of the Alloys of Silver, so that it will not be necessary to say anything about it in this place.

LUTES.

The term lute is derived from *lutum*, mud, and is used to express any substance employed for closing the joints of a chemical apparatus. The only lutes with which we have any concern at present, are the *fire-lutes*. These are used to secure the joints of apparatus subjected to high furnace-heats.

Parker's fire-lute is composed of clean clay 2 parts, sharp-washed sand 8 parts, horsedung 1 part. These are intimately mixed, and afterwards thoroughly tempered.

Watts's fire-lute is made of finely powdered porcelain clay, mixed to the consistence of thick paint, with a solution of borax, containing 2 ounces of borax to the pint of water.

Faraday's lute is made of the best Stourbridge clay, worked into a paste, and beaten till it is perfectly ductile and uniform. It is then flattened out into a cake, of such a size and shape as shall be most easily applied to the vessel to be coated. If this be a retort, it should be placed in the middle of a cake, which should be raised upon all sides, and gradually moulded and applied to the glass; if it be a tube, it should be laid upon one edge of the plate, and applied by rolling the tube forward. The surface to be coated should always be rubbed with a piece of the lute dipped in water, for the purpose of slightly moistening it and leaving a little of the earth on it. The lute should be pressed down so carefully as to exclude all air-bubbles, and the greatest care should be taken to join the edges properly, for which purpose they should be made thin by pressure, and also somewhat irregular in form.

The vessels, thus luted, should be placed in a warm situation,

and very gradually dried, being moved from time to time, so as to prevent irregularity.

The introduction of fibrous substances, so as to increase the tenacity by mechanical means, has been practised. Of these, horsedung, chopped hay and straw, horse and cow hair, and tow cut short, are most frequently employed. When used, they should be added in small quantity, and the mixture should contain more water and be more thoroughly and carefully mixed. It is best to add the fibrous substance to the dry clay, and to stir with a fork or pointed stick whilst the water is poured in, so as to obviate the necessity of using a great quantity of water. It ought to be as dry as possible, consistently with facility of working it. The wetter it is, the more liable it is to crack in drying.

Willis's cement, already spoken of, is made by dissolving one ounce of borax in half a pint of boiling water, and adding slaked lime enough to make a paste. This is to be spread over the vessel with a brush, and when it is dry, a coating of slaked lime and linseed oil is to be applied. It will dry in a day or two, and be fit for use.

FUEL.

The operations which we shall describe require, all of them, a very high temperature, which can only be obtained by the combination of oxygen with combustible substances. These combustibles are what we term fuel. There are some substances that are used in the small way, which properly come under this head, though not commonly known by that name. These are alcohol, wood-spirit, and the oils which are used in lamps for blowpipe purposes.

We have already spoken of these under the head of blowpipe operations. It is only necessary to compare their heating powers. Alcohol is the cleanest but weakest of the three. Pyroxylic spirit, which contains more carbon, gives a hotter flame, and oil is the hottest of the three.

Thus, one pound of *common alcohol* will, during its combus-

tion, raise 52.6 pounds of water from 0° to 212°, or will evaporate 9.56 pounds of boiling water; while *oil*, *wax*, or *tallow* will heat 78 pounds of water from 0° to 212°, and evaporate 14.18 pounds of boiling water. *Carburetted hydrogen gas* will heat 76 pounds of water from 0° to 212°, and will evaporate 13.81 pounds of boiling water.

The fuels used in furnaces are *wood*, *coal*, *charcoal*, and *coke*.

Wood.—This fuel is often employed in furnaces when a quick heat is desired. The amount of heat it yields will be considered when we speak of the relative value of different sorts of fuel.

Wood is composed of woody fibre, the constituents of the sap and water. The first, or *lignin*, is a compound of hydrogen, carbon, and oxygen, according to Prout, in the proportions $C_{12}H_8O_8$. Payen, however, divides it into two substances, *cellulose*, $C_{12}H_{10}O_{10}$; and *lignin*, $C_{35}H_{24}O_{20}$. The first of these constitutes the wall of the cells, and the second their contents. The earthy matters found in the ashes are contained in the sap, which also holds in solution the peculiar organic principles of the plant. The relative proportions of these ingredients have been found to vary with the season in which the wood has been cut. During the period of active growth they contain more water and sap than during the winter. The different parts of the plant also differ in this respect. Thus, the small shoots and twigs yield a larger percentage of water than the more solid stems.

Schübler and Hartig examined many varieties of wood, and found that the quantity of water varied from less than one-fifth to more than one-half of their weight. Thus, hornbeam contained 18.6, horse-chestnut 38.2, and black poplar 51.8% of water. According to Marcus Bull's experiments, green hickory loses 37½, white oak 41, and soft maple 38% by thorough drying.

Exposed to the air, wood loses water, and then it is said to be air-dried. It still, however, retains a notable quantity of water, as will be seen by the following table of some of the results of Count Rumford, who kept specimens of various air-dried woods at 277°, till they ceased to lose weight:—

100 parts of	oak wood	lost	16.64
"	elm	"	18.20
"	beech	"	18.56
"	maple	"	18.63
"	fir	"	17.53
"	birch	"	19.38
"	lime	"	18.79
"	poplar	"	19.55

Wood, in its green state, contains on an average about 42 per cent. of moisture, and after being air-dried for a year, from 20 to 25 per cent. According to Winkler, wood several years old, kept in a warm room for six months, contained 17 per cent. of water. Bull found that, after wood had been thoroughly dried, it would, in twelve months, absorb from the air of a room 10 per cent. of water.

A moment's consideration will convince any one that economy of fuel demands that wood should be used as dry as possible. All the water which is contained in it must be converted into steam at the expense of the fuel. Green wood contains 17% more water than seasoned wood. To convert this into steam, 6.8 pounds of dry wood are required. Estimating by weight, therefore, nearly one-fourth of the fuel is lost. If we estimate the loss by measure, as the water does not materially affect the bulk of the wood, we shall find that at least 10% is lost, by burning green instead of dry wood.

Woods are usually divided into two classes, *hard* and *soft*, names taken from their resistance to edge-tools, but answering very well to indicate their density and their power of calorification. Trees of the same species vary in density and hardness, according to the situation in which they are grown. Those growing on thin soils, in an exposed situation, are harder and denser than those more sheltered and grown on richer land.

Dry wood is much lighter than water, but this is due to the air contained in its cavities. When rasped, or filed, so as to destroy the pores, and thus deprive it of all but its natural buoyancy, the lightest wood is found to be denser than water.

By this treatment the specific gravities of the following woods is found to be—

Oak	1.27
Lime*	1.13
Fir	1.16
Beech	1.29

Long immersion in water deprives wood of its soluble and extractive matter, so that its calorifying powers are impaired.

Different kinds of wood do not differ very widely in their chemical composition, except as regards the inorganic matters contained in their ash. It is remarkable, however, that in all the varieties which have yet been examined, there is a slight excess of hydrogen over oxygen, though in woody fibres, the two elements are combined in the proportion to form water. Thus, Schädler and Petersen obtained results a few of which are given below.

	Carbon.	Hydrogen.	Oxygen.
Pure woody fibre	52.65	5.25	42.10
Quercus robur (oak)	49.43	6.07	44.50
Fagus sylvatica (beech)	48.53	6.30	45.17
Pinus abies (fir)	49.95	6.41	43.65

The ashes of wood vary not only with the species examined, but with the soil on which it grows. Generally, they consist of potash, soda, lime, magnesia, and iron combined with carbonic, silicic, sulphuric, and phosphoric acids, together with the chlorides of their radicals.

The amount of ash furnished by the different species varies very much. Thus Berthier found that fir yielded only 0.0083, while the linden or lime tree gave 1.05% of ash. The different parts of the tree also yield different quantities of ash, the bark and leaves yielding the most, the branches less, and the trunk least of all.

Turf and Peat.—These are the products of vegetable decomposition in low, moist places. Large quantities of water-plants

* *Tilia Europæa*, our common shade-tree, the linden.

spring up on these moors in the summer months, and in winter they die and fall upon the ground. They undergo decomposition, the gaseous matter escaping, and the greater portion of the carbon and the salts remaining.

In *turf*, the decomposition is not so complete as entirely to destroy the texture of the plants. Many twigs and roots still remain in it, and though dark-colored, it is, nevertheless, light and porous. In *peat*, all traces of vegetable form are lost, and the density of the mass is very much increased.

The proportion of ash varies from 4.61 to 33%. The quantity of hydrogen and oxygen is very variable. The average percentage of carbon is about 57.5.

Coal.—The geological situations of coal are in the *tertiary* and *secondary formations* and in the *coal measures*, which lie between the new red sandstone and the carboniferous limestone.

Lignite.—This is found in tertiary formations, and divisible into several varieties, such as *brown coal*, *bituminous wood*, *common earthy lignite*. Of these, the *brown coal* resembles turf, and loses about 20% of water on thorough drying, and yields 35 to 40% of a coke resembling charcoal. *Bituminous wood* is softer, retains to a certain extent its woody character, but is dark-brown or black, and more nearly resembles asphaltum or mineral pitch than the wood from which it is formed. *Common lignite* resembles coal from the secondary formations. It is usually black or brown, with a compact structure and an irregular fracture. When heated it gives off inflammable gases, together with acid and tarry matter; and the resulting coke usually retains the form of the fragment from which it was produced. *Earthy lignites*, as their name implies, contain foreign matters, the principal of which are clay and iron pyrites.

In the United States, the chief deposit of this coal is near Richmond. The proportion of ash varies greatly, the earthy lignites of course yielding the most. Thus, lignite from Laubach, contains only 0.49% of ash, while that of Meiszner has 19.1%. The formula of lignite free from bitumen has been stated at $C_{33}H_{21}O_{16}$.

Mineral Coal.—In this variety of coal, all traces of vegetable tissue have disappeared, though impressions of plants are always

found among the shales which cover the beds. There are two varieties of mineral coal, the bituminous or pit coal, and anthracite.

Pit Coal, Bituminous Coal.—This coal is found in compact masses or great beds interstratified with earthy matters. It is black, sometimes dull, but often has a glassy, and sometimes an iridescent lustre, and a conchoidal or hackly fracture. The black and shining variety with a conchoidal fracture is rich in carbon, while that which is dull and brown contains less of that element.

The physical characters of coal have furnished a basis for the classification of the different varieties. That which is compact and has a resinous lustre is called *pitch coal.* When it has a cubical fracture, it is called *cubical* or *cherry coal.* When it melts and agglomerates in the fire, it is termed *caking coal;* and when it can be easily split in leaves parallel to the surface of deposition, it is called *slate* or *splint coal.*

The average specific gravity of bituminous coal is about 1.3.

Anthracite.—This is the most solid and compact of the coals. Its specific gravity varies from 1.343 to 1.751. It forms thick, continuous beds of great extent. It is black, with a shining, sometimes almost metallic lustre, with occasionally a brilliant iridescence. Its fracture is more irregular than that of pit-coal, and is usually conchoidal. It is the hardest and toughest of all the coals, kindles with more difficulty, but burns readily in masses, with little flame, and throws out an intense heat.

The following table of analyses by Regnault and Richardson, exhibits the difference in the chemical composition of coals:—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ash.
Turf . . .	58.09	5.93	31.37	4.61
Lignite . .	71.71	4.85	21.67	1.77
Splint Coal . .	82.92	6.49	10.86	0.13
Cannel . .	83.75	5.66	8.04	2.55
Cherry Coal .	84.84	5.05	8.43	1.68
Caking Coal .	87.95	5.24	5.41	1.40
Anthracite . .	91.98	3.92	3.16	0.94

The influence of heat on fuel is, of course, to decompose it, but the products of this decomposition, when air is excluded and when it is freely admitted, differ very widely.

When air is excluded, as in dry distillation, the volatile and combustible products of the decomposition may be collected. Under the influence of a high heat, hydrogen and oxygen are of course volatilized, but they do not pass over as pure gases. Much of the oxygen combines with the hydrogen to form water. A portion of it unites with the carbon, and still more of it with the carbo-hydrogens, formed from the excess of hydrogen, which always exists in fuel. Thus, we have a series of compounds continually varying with the variable amounts of these three elements. The permanently gaseous products are usually carbo-hydrogens only; but besides these, the dry distillation of fuels affords *acetic* and other acids, *pyroxylic spirit*, creosote, tar, and a very great variety of substances allied to petroleum, as well as such solids as naphthaline and paraffine.

When air is freely admitted, however, these volatile products, already at a high temperature, are rapidly consumed; so that, with the exception of carbon and a few unconsumed products of decomposition, which go up as soot, the whole combustible matter is resolved into carbonic acid and water.

These natural fuels are often treated so as to get a more economical fuel in a given bulk. Thus wood, containing, as we have seen, after the most thorough drying, a large quantity of water, must necessarily lose a great deal of its calorific power. When, however, it is converted into charcoal, this source of loss is avoided, and a fuel is obtained of which a given bulk is capable of evolving a far greater quantity of caloric.

Charcoal.—When wood is ignited, and then excluded from the air while burning, its volatile products are driven off by the slow combustion which continues for a short time, and its carbon is left behind. Some of the latter, however, is necessarily lost in consequence of its having been consumed to furnish the heat which has driven off the volatile products. If, however, it be heated at once in a close vessel, these products are driven off without loss of carbon. The difference between the charcoal yielded by these two processes is very great. Karsten found that pine,

which gave only 13.75% of charcoal by the process of quick-charring, yielded 25.95 by the slow process.

Charcoal is commonly made by building the wood into piles of peculiar construction, covered with turf, so as to admit only air enough for a very slow combustion. At first, a yellow smoke escapes, which contains the volatile products first formed, mixed with much watery vapor, but gradually the color of the smoke changes to a clearer blue, showing that the water is nearly expelled. At this period the openings are all closed, and the wood is allowed to char.

This process is liable to the objection that it wastes the volatile products, which are often very valuable. To obviate this, furnaces have been constructed, which are provided with tubes and vessels to carry off and condense these volatile substances. Some of these furnaces are, like the charcoal mounds, heated by the wood itself. Others are cylindrical ovens heated by an external fire, or, after the process commences, by the gas which comes off from the charring wood.

The average quantity of charcoal produced in mounds amounts to about 22%. The furnaces yield 27%, but it requires about 5% to heat them, so that the gain is only represented by the volatile products which have been saved.

The specific gravity of charcoal varies with that of the wood from which it has been taken. Thus, Knapp found that a cubic foot of beech-wood charcoal weighed from 8 to 9 pounds; of oak charcoal, 7 to 8 pounds; of pine charcoal, 5.5 to 7 pounds, and of the charcoal from the softer woods, from 4.5 to 5.5 pounds.

The charcoal obtained by these processes is not absolutely pure carbon, as by heating them, about 7 per cent. of volatile matter can still be driven off.

Charcoal is a powerful absorbent. It abstracts a large quantity of water from the atmosphere, and absorbs gases with great energy. Its strongest affinity is for ammoniacal gas, of which it absorbs 90%; its weakest is for hydrogen, of which it only absorbs 1.75%.

There is a point at which the charring process should stop. If carried too far, loss will be sustained. Thus, Berthier found

that if a cubic foot of wood contains a weight of combustible matter represented by 908—

1	cubic foot	charred	during	3	hours	will contain	883 parts.
1	"	"		4	"	"	904 "
1	"	"		5	"	"	1133 "
1	"	"		$5\frac{1}{2}$	"	"	1091 "
1	"	"		$6\frac{1}{2}$	"	"	1136 "
1	"	mound charcoal,				will contain	1069 "

It follows, from the above table, that the process of charring may be advantageously checked before complete carbonization is attained. In France and Belgium, a great saving is effected by using wood thus imperfectly charred. It is called *charbon roux*. The objection to it is that it is very difficult to secure anything like uniformity in the quality of the article.

Peat charcoal is often used in Europe. A given weight of lignite produces more charcoal than the same weight of wood, for reasons which are too manifest to need rehearsing.

Coke.—Coke bears the same relation to bituminous coal that charcoal does to wood. It generally contains more combustible matter in the same bulk than the coal from which it has been obtained. It should be solid enough not to crush easily, and should come in tolerably large pieces. Spongy coke, easily crushed, is not an economical fuel.

Like charcoal, coke is made in heaps or in ovens. In this country, most if not all of the coke which is used is obtained from gas-houses, and as refuse from furnaces heated by bituminous coal.

On cooling, good coke splits into long prismatic masses, not unlike basaltic columns. Its color is a steel-gray, at times approaching a silvery whiteness, and having now and then a metallic lustre. Some varieties are iridescent, an appearance which is believed to depend upon the presence of sulphur. Like charcoal, coke absorbs moisture from the atmosphere. In damp weather, this hygrometric water is sometimes as much as 30 per cent. After long exposure to moisture, coke becomes soft and friable, and becomes worthless for some of the purposes to which it has been applied.

Comparative Value of Fuels.—The different fuels which have been enumerated vary very greatly in their heating powers. Different methods have been adopted to determine the calorific energy of different sorts of fuel. The object is to ascertain the amount of heat produced and the time required to generate it. Now, as it is impossible to estimate the amount of heat actually produced, the results of the caloric, or its effects, or something else have been chosen as indicating as nearly as possible the relative value of fuels.

The instrument by which these effects are determined is called a calorimeter, and the heat is measured either by the quantity of ice melted, or the weight of water elevated to a given temperature, or evaporated by the substance operated upon. Another method is to determine the period during which an apartment may be kept at a given temperature. It was this latter method which was adopted by Marcus Bull, in his admirable researches, a table of the results of which we subjoin:—

	Specific gravity of dry wood.	Avoirdupois pounds in cord of dry wood.	Product of charcoal from 100 pts. of dry wood, by weight.	Specific gravity of dry coal.	Pounds of dry coal in one bushel.	Pounds of charcoal from one cord of dry wood.	Bushels of charcoal from one cord of dry wood.	Time 10° of heat were maintained by one pound.		Value of specified quantities of shell-bark hickory = 100.
								h.	m.	Cord.
White ash (*Fraxinus Americana*)	.772	3450	25.74	.547	28.78	888	31	6	40	77
Apple-tree (*Pyrus malus*)	.697	3115	25.00	.445	23.41	779	33	6	40	70
White beech (*Fagus sylvestris*)	.724	3236	19.62	.518	27.26	685	23	6		65
Black birch (*Betula buta*)	.697	3115	19.40	.428	22.52	604	27	6		63
White birch (*Betula populifolia*)	.530	2369	19.00	.364	19.15	450	24	6		48
Butternut (*Juglans cathartica*	.567	2534	20.79	.287	12.47	527	42	6		51
Red cedar (*Juniperus Virginiana*)	.565	2525	24.72	.288	12.52	624	50	6	40	56
American chestnut (*Castanea vesca*)	.522	2333	25.29	.379	19.94	590	30	6	40	52
Wild cherry (*Cerasus Virginiana*)	.597	2668	21.70	.411	21.63	579	27	6	10	55
Dogwood (*Cornus florida*)	.815	3643	21.00	.550	28.94	765	26	6	10	75
White elm (*Ulmus Americana*)	.580	2592	24.85	.357	18.79	644	34	6	40	58
Sour gum (*Nyssa sylvatica*)	.703	3142	22.16	.400	21.05	696	33	6	20	67
Sweet gum (*Liquidambar styraciflua*)	.634	2834	19.69	.413	21.73	558	26	6		57
Shell-bark hickory (*Carya squamosa*)	1.000	4469	26.22	.625	32.89	1172	36	6	40	100
Pig-nut hickory (*Carya porcina*)	.949	4241	25.22	.637	33.52	1070	32	6	40	95
Red-heart hickory	.829	3705	22.90	.509	26.78	848	32	6	30	81
Witch hazel (*Hamamelis Virginica*)	.784	3505	21.40	.368	19.36	759	39	6	10	72
American holly (*Ilex opaca*)	.602	2691	22.77	.374	19.68	613	31	6	20	57
American hornbean (*Carpinus Americana*)	.720	3218	19.00	.455	23.94	611	25	6		65
Laurel (*Kalmia latifolia*)	.663	2963	24.02	.457	24.05	712	30	6	40	66
Hard maple (*Acer saccharinum*)	.644	2878	21.43	.431	22.68	617	27	6	10	60
Soft maple (*Acer rubrum*)	.597	2668	20.64	.370	19.47	551	28	6		54
Large magnolia (*Magnolia grandiflora*)	.605	2704	21.59	.406	21.36	584	27	6	10	56
Chestnut white oak (*Quercus prinos palustris*)	.885	3955	22.76	.481	25.31	900	36	6	30	86
White oak (*Q. alba*)	.855	3821	21.62	.401	21.10	826	39	6	20	81
Shell-bark white oak (*Q. obtusa*)	.775	3464	21.50	.437	22.99	745	32	6	20	74
Scrub oak (*Q. catesbæi*)	.747	3339	23.17	.392	20.63	774	38	6	30	73
Pin oak (*Q. palustris*)	.747	3339	22.22	.436	22.94	742	32	6	20	71
Scrub black oak (*Q. barristeri*)	.728	3254	23.80	.387	20.36	774	38	6	30	71
Red oak (*Q. rubra*)	.728	3254	22.43	.400	21.05	630	30	6	20	69

	Specific gravity of dry wood.	Avoirdupois pounds in cord of dry wood.	Product of charcoal from 100 pts. of dry wood, by weight.	Specific gravity of dry coal.	Pounds of dry coal in one bushel.	Pounds of charcoal from one cord of dry wood.	Bushels of charcoal from one cord of dry wood.	Time 10° of heat were maintained by one pound.	Value of specified quantities of shell-bark hickory = 100.
								h. m.	Cord.
Barren oak (*Q. ferruginea*)	.694	3102	22.37	.447	23.52	694	29	6 20	66
Rock chestnut oak (*Q. montana*)	.678	3030	20.86	.436	22.94	632	28	6	61
Yellow oak (*Q. acuminata*)	.653	2919	21.60	.295	15.52	631	41	6 10	60
Spanish oak (*Q. falcata*)	.548	2499	22.95	.362	19.05	562	30	6 20	52
Persimmon (*Diospyros Virginiana*)	.711	3178	23.44	.469	24.68	745	30	6 30	69
Yellow pine, soft (*Pinus variabilis*)	.551	2463	23.75	.333	17.52	585	33	6 30	54
Jersey pine (*P. inops*)	.478	2137	24.88	.385	20.26	532	26	6 40	48
Pitch pine (*P. rigida*)	.426	1904	26.76	.298	15.68	510	33	6 40	43
White pine (*P. strobus*)	.418	1868	24.35	.293	10.42	455	30	6 40	42
Yellow poplar (*Liriodendron tulipifera*)	.563	2516	21.81	.383	20.15	549	27	6 10	52
Lombardy poplar (*Populus dilatata*)	.397	1774	25.00	.245	12.89	444	34	6 40	40
Sassafras (*Laurus sassafras*)	.618	2762	22.58	.427	22.47	624	28	6 20	59
Wild service (*Aronia arborea*)	.887	3964	22.62	.594	31.26	897	29	6 20	84
Sycamore (*Platanus occidentalis*)	.535	2391	23.60	.374	19.68	564	29	6 40	52
Black walnut (*Juglans nigra*)	.681	3044	22.56	.418	22.00	687	31	6 20	65
Swamp Whortleberry (*Vaccinium corymbosum*)	.752	3361	23.30	.505	26.57	783	29	6 30	73
									Ton.
Lehigh coal				1.494	78.61			13 10	99
Lackawanna coal				1.400	73.67			13 10	99
Rhode Island coal				1.438	75.67			9 30	71
Schuylkill coal				1.453	76.46			13 40	103
Susquehanna coal				1.373	72.25			13 10	99
Swatara coal				1.459	76.77			11 20	85
Worcester coal				2.104	110.71			7 50	59
									100 bu.
Cannel coal				1.240	62.25			10 30	230
Liverpool coal				1.331	70.04			9 10	215
Newcastle coal				1.204	63.35			9 20	198
Scotch coal				1.140	59.99			9 30	191
Karthaus coal				1.263	66.46			9 20	208
Richmond coal				1.246	65.56			9 20	205
Stony Creek coal				1.396	73.46			9 50	243
Hickory charcoal				.625	32.89			15	166
Maple charcoal				.431	22.68			15	114
Oak charcoal				.401	21.10			15	106
Pine charcoal				.285	15.00			15	75
Coke				.557	20.31			12 50	126
Composition, 2 parts Lehigh, 1 charcoal, 1 clay, by weight								13 20	

Another very ingenious method has been suggested by Berthier. He bases his process upon a discovery of Welter, that the amount of heat produced by burning bodies is in direct proportion to the quantity of oxygen required to effect their combustion. He mixes intimately with litharge a known weight of the substance in fine powder, and heats it in a closed crucible. The oxygen of the litharge combines with the combustible, and lead sinks to the bottom in a button. A comparison of the weight of one button with that of another affords an estimate of the value of the tested articles as fuel. Carbon, which, according to Despretz, affords 34.5 parts of metallic lead, is selected as the standard of comparison. It must be borne in mind, in these investigations, that the reducing power of hydrogen is more than three times as great as that of carbon. Forgetfulness of this will lead to grave errors in the estimation of the results obtained.

Ure, whose results differ very widely from Berthier's, and from those of other chemists who have adopted this method, expresses a total want of confidence in it. He found that 1 part of charcoal produced 60.3 parts of lead; whereas, according to Berthier and Despretz, but 34.5 were possible.

It may be that, in these experiments of Ure's, some sulphuret of iron was present, which would in part account for this great difference.

It must be borne in mind that the theoretical results obtained by these processes differ somewhat from those actually arrived at in practice. This depends upon a variety of circumstances, the arrangements of the furnaces, the extent of the surface to be heated, the manner in which the heat is applied, &c.

Time is a very important element in the estimation of the effect of fuel. For some purposes a rapid heat is desirable. The lighter woods, which contain much hydrogen, will be applicable to these. As a general thing, however, the more slowly burning fuels are the best, because it takes time for the substances to be heated to absorb the necessary amount of caloric.

The freedom of the circulation of air is another most important element of the heating powers of a fuel. A full supply of oxygen is necessary for the perfect evolution of the entire amount

of heat of which any fuel is capable. Any defect in the bars of the furnace, or in the structure of a chimney, will consequently materially interfere with the perfect combustion of the fuel.

The size of the pieces introduced into the furnace will, for the same reason, affect the combustion. If they are too large, they will absorb too much heat, and will consequently lose caloric. If too small, they will burn too rapidly. When, however, they are extremely small, they fall together and choke up the draught, so that the mass only smoulders, like tan in a fireplace.

Practically, for the purposes of the chemist, the best fuel is charcoal or coke, or a mixture of the two. The ash of charcoal being infusible, it passes through the bars of the grate as a white powder. Should potash, however, be in large excess, it corrodes the bricks, by forming with them a silicate of potash, which runs down the walls and chokes the bars. In small quantities, this action is beneficial, as it furnishes a protective varnish, and unites the bricks and lutes, by forming a sort of cement, which intimately combines with them.

Coke contains a very variable amount of ash, which is composed chiefly of oxide of iron and clay. The latter is not fusible by itself, but may soften. When pure, it forms a harmless slag, which injures neither the furnace nor the crucibles. Usually, however, the oxide of iron predominates. In this case the ash is very injurious, for it is reduced to a protoxide, which is not only fusible, but powerfully corrosive to all argillaceous matters, so that both the crucibles and the furnaces suffer.

Coal, of course, is liable to all the objections which can be urged against coke, and the presence of sulphur in it increases the difficulties. Bituminous coal should never be used in crucible operations, because it swells so as to be very troublesome. Anthracite may be used if carefully selected. It is unnecessary to say that it must be perfectly free from slate, must yield an infusible ash, and be as clean as possible. It is, however, as far as the author's experience goes, decidedly inferior to either coke or charcoal. Some of the softer varieties of it are very bad, so imperfectly have they been cleansed. The author has seen broad, thick cakes, of a very clear pale-green glass, formed from some of these coals in the furnace.

Weight for weight, coke and charcoal give out about equal heat. But, bulk for bulk, coke, being denser than charcoal, possesses a greater calorifying power. At high temperatures, this difference amounts to as much as 10 per cent. in favor of coke. Coke, however, is difficult to kindle, and, for its perfect combustion, requires a strong draught.

From what has already been said, it will be seen that fuel should not be thrown at random into the furnaces, but should be carefully selected, so that the pieces shall be nearly uniform in size. If there is much dust in the coke or coal, it will, as we have already seen, fill up the interstices between the pieces and choke the draught. If the fuel be too large, the heating will go on too slowly. Coal or coke, for ordinary crucible operations, should be broken as nearly as possible into cubes of an inch or an inch and a quarter on a side.

MEASUREMENT OF THE HEAT OF FURNACES.

Instruments used for the purpose of estimating the high heats produced by furnaces have been called *pyrometers*. Of these, there are two which have attracted special attention, one invented by Wedgewood and the other by Daniell.

Wedgewood's pyrometer consisted of a gauge and pieces of clay. The gauge is a plate of brass, with two rulers of the same substance firmly fixed in it. These gradually approach one another in the diameter of the space inclosed by them, the entire diminution amounting to two-tenths of an inch. The test-pieces are made of clay, finely powdered, sifted, and mixed with water, and then passed through an iron tube and cut into cylinders of a suitable length. When dry, they are carefully adapted to the zero of the gauge. One of two of these is put into the furnace and heated to the full power of the fire. It is then withdrawn, placed between the rulers, and pushed on till it is stopped by the narrowness of the passage. The degree of heat is then calculated from the contraction it has undergone.

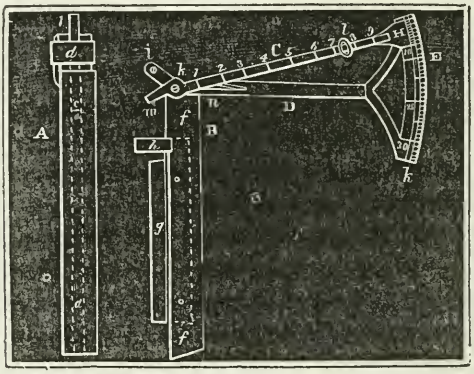
This process is objectionable on account of the material selected for the test-pieces. Clay contracts as powerfully when subjected for a long time to a low heat as when exposed for a

shorter period to a higher one. Consequently, the results obtained by Wedgewood's instrument are enormous exaggerations. Thus, he sets down the melting-point of cast-iron at 17,977° of Fahrenheit, whereas in fact it is only 2,786°.

Guyton suggested a pyrometer to obviate these difficulties, and Daniell constructed a very finished one, on the principle laid down by the French chemist.

"It consists of two parts, which may be distinguished as the register, 1, and the scale, 2, Fig. 50. The register, A, is a solid

Fig. 50.



bar of black-lead earthenware highly baked. In this a hole, *a a*, is drilled, into which a bar of any metal, six inches long, may be dropped, and which will then rest upon its solid end. A cylindrical piece of porcelain, *c*, called the index, is then placed upon the top of the bar, and confined in its place by a ring or strap of platinum, *d*, passing round the top of the register, which is partly cut away at the top, and tightened by a wedge of porcelain, *e*. When such an arrangement is exposed to a high temperature, it is obvious that the expansion of the metallic bar will force the index forward to the amount of the excess of its expansion over that of the black-lead, and that when again cooled it will be left at the point of greatest elongation. What is now required is the measurement of the distance which the index has been thrust forward from its first position, and this,

though in any case but small, may be effected with great precision by means of the scale.

"This is independent of the register, and consists of two rules of brass, *f f*, and *g*, accurately joined together at a right angle by their edges, and fitting square upon two sides of the black-lead bar. At one end of this double rule, a small plate of brass, *h*, projects at a right angle, which may be brought down upon the shoulder of the register formed by the notch cut away for the reception of the index. A movable arm, D, is attached to this frame, turning at its fixed extremity on a centre *i*, and at its other end carrying the arc of a circle, whose radius is exactly five inches, accurately divided into degrees, and thirds of a degree. Upon this arm, at the centre of the circle *k*, another lighter arm, C, is made to turn, one end of which carries a nonius, H, with it, which moves upon the face of the arc, and subdivides the former graduation into minutes of a degree; the other end crosses the centre, and terminates in an obtuse steel point *m*, turned inwards at a right angle.

"When an observation is to be made, a bar of platinum or malleable iron is placed in the cavity of the register; the index is to be pressed down upon it and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross-piece upon the shoulder, and placing the movable arm so that the steel part of the radius may drop into a small cavity made for its reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted which the nonius indicates upon the arc. A similar observation must be made after the register has been exposed to the increased temperature which it is designed to measure, and again cooled, and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of this pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, the temperature of which is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of

degrees is thus determined, and the value of all other expansion may be considered as proportionate."

The following is a list of the melting-points of some of the metals; and it is obvious that, in an assay of each particular metal, the temperature employed must exceed by a considerable number of degrees its melting-point. The table is, therefore, very useful.

	Fahrenheit.
Tin melts at	422°
Bismuth	497
Lead	612
Zinc	773
Cadmium	442
Silver	1,860
Copper	1,996
Gold	2,016
Cast-iron	2,786

Cobalt and nickel rather less fusible than iron.

Daniell.

CHAPTER II.

GOLD.

Gold is one of the longest known of all the metals. Being usually found native, and capable of being smelted in a rude way without difficulty, it is well adapted to attract the attention of the savage and excite his cupidity; while its rarity, as well as its intrinsic value, gives it a most powerful influence over civilized man.

It is occasionally found crystallized in octahedra, cubes, and allied forms. These, however, are not absolutely pure, but usually contain silver and sometimes copper, and that too in no definite proportion, as will be seen by the following table, the

first and second analyses in which have been made by Boussingault, and the others by Rose :—

		Gold.	Silver.
1.	Crystal from Transylvania	64.52	35.84
2.	" Marmato	73.45	26.48
3.	" Titiribi	76.41	23.12
4.	" Beresow	91.88	8.03
5.	" Katharinenburg	93.34	6.28

Awdejew found the silver in the crystals from Katharinenburg to vary from 3.86 to 28.3 per cent. Gold is more commonly found in spangles, rolled grains, laminæ, masses of variable size, irregular or arborescent, and in threads of various sizes twisted into a chain of minute octahedral crystals.

Its geological situations are the crystalline primitive rocks, the compact transition rocks, the trachytic and trap rocks, and alluvial grounds. It never is found constituting a vein by itself, like the baser metals. It is disseminated through the rocky masses, or spread out on their surface, or imbedded in their cavities. The minerals composing the veins are usually either quartz, calcspar, or sulphate of baryta. The gold may either be directly imbedded in these minerals, as, for example, in the quartz of California, or it may be distributed through masses of other ores contained in the veins, as in the iron pyrites of Virginia, or it may be combined with another metal as a sort of natural alloy, as in the telluret and the sulpho-plumbiferous telluret of gold of Nagyag in Transylvania. The most common ores containing gold are iron, copper, and arsenical pyrites, galena, and blende (sulphuret of zinc). In the auriferous pyrites the gold is commonly invisible till the ore is roasted, after which the bright spangles of the precious metal can be easily detected by the naked eye, even, it is said, when they amount to no more than the five-millionth part of the entire weight of the ore.

In the primitive rocks, gold occurs, disseminated in small grains, spangles, and crystals. In secondary rocks it has not been found, but it exists in considerable quantity in trap. Thus, in Hungary, Transylvania, and South America, trachyte is the gold-bearing rock. The primary source of the metal is supposed

to be in the sienite and greenstone porphyry, which underlie the igneous rocks. In alluvial grounds, gold is more commonly found than anywhere else. It is there disseminated in spangles through the sands of certain plains and rivers, especially in their re-entering angles, at low water, and after storms and floods. It was formerly supposed that the gold was washed down from the mountains where the rivers originated, but good reasons have been given for believing that it comes from the plains through which these streams cut their way. On the coast of California, this metal is found in the sands of the ocean, at a little distance from the shore. For miles along the coast to the north of San Francisco, the lead used for soundings brings up a black heavy sand, which contains spangles of gold. Gold is also found in pebbles in tertiary strata. I have in my possession a fragment of beautiful native gold, which was taken out of a quartz pebble picked up among a host of similar rolled pebbles, on one of the gravel hills in the city of Baltimore. The metal, as originally broken out of the stone, weighed about two pennyweights. Other pebbles were found in the same hill, containing small spangles of the precious metal.

The geographical distribution of gold is very extensive. The most important European mines are those of Hungary and Transylvania, and those worked by Russia in the Ural mountains. In Asia, the mines of this metal are numerous and productive. Japan, Formosa, Ceylon, Java, Sumatra, Borneo, and other islands of the Indian Archipelago abound in the precious metal. Africa, the ancient country of gold, still produces it. The gold of Kordofan, the Gold Coast, and Sofala may be named. Washings are common in Virginia and North Carolina, Mexico, and some of the South American States also furnish this metal. But all other gold countries in the world must yield to the superior productiveness of California and Australia.

METALLURGIC TREATMENT OF GOLD ORES.

Washing.—The metallurgic treatment of gold varies of course with the circumstances under which it is obtained. The rudest method is what is known in Virginia and North Carolina as

"panning out." It consists simply in agitating the sand in a pan with water, washing off the lighter particles of earth till the gold, from its greater specific gravity, is left nearly pure at the bottom of the pan. Fusion with some suitable flux completes the reduction.

In Hungary, this method is somewhat modified. A plank, with twenty-four transverse grooves, is held in an oblique position. In the first of these grooves the auriferous sands are placed; water is then thrown over them till the greater part of the sand is washed away. The gold, mixed with the minimum of sand, collects in the lower grooves, whence it is removed into a flat wooden basin, and, by a peculiar sleight-of-hand, acquired by long practice, the metal is entirely separated. These operations remove the larger spangles of gold; the smaller particles are extracted by amalgamation.

In our gold works, the processes of washing and amalgamation are sometimes performed together. The *cradle* is one of the forms of apparatus which is thus applied. This is a swinging trough, the motion of which resembles that of the piece of furniture from which it takes its name. The trough is divided by a grating into two compartments, the lower of which contains the mercury, and the upper the ore. While the instrument is agitated, a stream of water pours over the ore, and sweeps off the lighter sand, while the gold, with a portion of the earthy matter, drops through the grating into the mercurial bath, where it is amalgamated.

Stamping.—This process is used to reduce the coarser sand ores and the rocks which contain gold to a sufficient fineness to enable the workmen to wash with advantage, or to use any other metallurgic method of separating the metal. High hopes were entertained of the results of this process applied to the gold-bearing quartz of California, but these expectations have been very generally disappointed. But one or two of the numerous stamping-mills erected in that land of gold have paid their expenses. This unfortunate result is to be attributed to a variety of causes. Incompetence in the superintendents of the mills, injudicious selection of localities, the high price of labor, the great irregularity and uncertainty of the supply of water, are

some of the elements of this failure. The operations of stamping and washing are often performed at the same time, a stream of water sweeping over the ore while it is being pulverized, and carrying it over hides or blankets. Upon the rough surfaces of these the gold, mixed with some sand, is deposited.

The auriferous sulphurets of the baser metals must be managed in a different manner. When properly treated, they yield a good interest on the money and labor invested, though, as a general thing, they are much poorer than the last-named ores. Some contain only one two-hundred-thousandth part of gold, and yet have been worked to advantage. They are first roasted in the open air, or in a calciner with a draught over its bed, in order to drive off sulphur, and peroxidize the metals. In some establishments, the oxidation is effected at the common temperature of the atmosphere, the action of the oxygen being facilitated by the admixture of common salt with the finely comminuted ore. After this, some rely on washing (an imperfect process), to separate the gold.

Fusion.—Rich ores of gold, in which there is no alkaline sulphuret to dissolve the sulphuret of the metal, may be directly fused with any thin flux, that will sufficiently act upon the stony matters of the gangue.

Fusion is used with two objects; the one is to separate the metals from adhering stone, the other to smelt out a metallic mass which can be directly cupelled. The rich *mattes* (metallic oxides and sulphurets containing metal) obtained by the first fusion, are again roasted to complete the oxidation of the baser metals. The calcined mass is then fused with lead, which combines with the gold, and is separated from it by cupellation. Gold ore, containing much copper, is better treated by amalgamation.

Cupellation.—The rationale of this process is very simple. It depends upon the tendency of some metallic oxides to run through a porous substance which remains impermeable to the purer unoxidated metals. It is a cheap, rapid, and, if properly conducted, certain method of purifying the noble metals. It will be treated of under the head of the Metallurgy of Alloys of Silver.

Amalgamation.—Mercury has a powerful affinity for most

metals, forming an amalgam, when fairly brought in contact with them. This property of mercury is taken advantage of by those who work in the precious metals. Formerly much mercury was lost in consequence of the careless manner in which it was used. At present, however, the process is better understood, and its results are more favorable. The mode commonly employed is that of revolving barrels. The ore is introduced into the barrels, and they are made to revolve rapidly till the gold is all taken up. The liquid amalgam is then allowed to settle down in the barrels, when it is drawn off, and pressed in bags of strong fine canvas, of chamois leather, or of buckskin. In this manner the excess of mercury is forced out through the pores of the bag, and there is left behind a pasty amalgam. This is decomposed by distillation in cast-iron retorts, by means of which the mercury is drawn over, and the gold remains in the retort in a spongy state. The gold thus obtained is usually free from all foreign metals except silver. This is easily separated from the alloy by the operation of parting.

In the Southern States of our Union, some difficulty is experienced in managing amalgamation with economy. The deeper ores are all decidedly pyritous, and, independently of the loss of mercury by its combination with sulphur, the particles of gold are so protected and shielded from the action of the liquid metal that but a fraction of what the ore actually contains is extracted. Gold ore, for example, containing from thirty to seventy dollars' worth of metal to the ton, is crushed, oxidated, and amalgamated. Only a portion of the gold is thus obtained. The residual ore is then exposed again to the action of the atmosphere for a year, and so more deeply oxidated. It is then again amalgamated, and I have been assured by gold miners in Virginia, that they have obtained more gold from the second than from the first amalgamation. These operations are sometimes repeated four or five times, more or less metal being obtained at every repetition. This is very expensive, and the poorer varieties of ore will not pay for roasting by the fire.

It is hardly necessary to add that the quicksilver must be used in considerable excess, for, should it become pasty, it will

not absorb the gold, and will, besides, be difficult to separate from the pounded ore with which it is mixed.

METALLURGY OF THE ALLOYS OF GOLD.

The purification of alloys of gold, or rather the separation of other metals from gold, is effected either in the wet or the dry way. The latter is the mode most frequently adopted for the separation of the more common metals.

The fragments of gold swept up in the goldsmith's shop, or in the mechanical room of a dentist, are mixed with many other metals, and with earthy and other impurities. The latter are got rid of, in part, by washing; the former separated by fusion with oxidating reagents. These are numerous, but the most energetic of them are litharge and nitre.

The nitrates of potash and soda are easily decomposable at a full red heat. They lose oxygen, and are converted into nitrites. The oxygen contained by these salts being in large proportion and easily separable, they readily communicate it to the oxidable metals fused with them. The oxides formed in this manner enter into fusion, and, being lighter than the metals to be refined, float on the surface of the metallic bath in a slag, of a fluidity and brightness corresponding to the amount of the flux. Schlutter used, for this poor refuse, mixtures of glass with carbonate of potassa, litharge, and granulated lead. Borax constitutes another valuable addition to these oxidating reagents, because, while it possesses considerable oxidating powers, it has also the advantage of being an universal flux, and is, consequently, particularly applicable to refining processes in which the operator is compelled to contend with earthy impurities.

Scorification.—This is a process which furnishes an alloy well adapted for cupellation, while it oxidates the baser metals. It will be described under the head of Alloys of Silver. We will only say that, when this process is adopted, it must be pushed to the thorough removal of all tin and zinc, because the cupellation would otherwise be ruined, the gold being projected by the violence of the ebullition.

Tin is a particularly troublesome component of a gold alloy,

as the smallest quantity of it communicates the most intractable character to this metal. It gives it a remarkable hardness and brittleness. The mere exposure of a bar of gold to the vapors arising from a bath of redhot tin, is sufficient to destroy its malleability and make it brittle. This impurity is easily got rid of by fusion with corrosive sublimate or with nitre. The first of these agents converts the metal into the volatile perchloride of tin, which passes off with the mercury in vapor, leaving the metallic bath entirely free from tin. The second removes it by oxidating it to stannic acid, so that it is all contained in the slag, which consists chiefly of stannate of potash.

Sulphuret of Antimony.—Sulphuret of antimony, or *crude antimony*, as it is called in commerce, is one of our most powerful means of separating gold from its alloys. Iron, tin, zinc, and even silver are got rid of by means of this reagent, which is a favorite one with goldsmiths who wish to bring their gold to a very high standard. The alloy is heated in a crucible, and, when in a state of perfect fusion, from twice to four times its weight of very pure sulphuret of antimony is carefully thrown upon it. To this some add sulphur, when the quantity of silver in the alloy exceeds one-third. It must be heated moderately, to avoid spirting, and the melting substance must be sedulously guarded against the accidental intrusion of cinders from the fire. Should a fragment of coal fall in, a violent effervescence will take place, which will throw the contents of the crucible over its sides and cause great loss. The crucible, to avoid loss, should be so large that the alloy and the crude antimony will not occupy more than two-thirds of its cavity. The foreign metals all unite with the sulphur, and the gold, alloyed with the antimony, sinks to the bottom. When the fusion has become perfectly tranquil, the mixture is poured into a conical ingot-mould of iron, in which the same stratification of the alloys and the sulphurets takes place. The fusion is repeated with fresh quantities of sulphuret of antimony as often as may be judged necessary.

The antimony must now be separated from the alloy. For this purpose it may be roasted in a muffle, and then smelted with borax, nitre, and glass; two parts of the first to one of

each of the others. By this process, however, gold is lost. A more efficient roasting is accomplished in the following manner: The gold is fused in a crucible, and, when well heated, the blast from a pair of bellows is thrown upon it. At first it is necessary to be very cautious, as too great a draught hurries the volatilization of the antimony, so that some gold is carried off with it. The current of air should be just strong enough to produce visible fumes. When the gold is nearly pure, it seems to thicken and is covered with a film. The heat is then increased and the crucible closed for a short time. The cover is now taken off, and a current of air again driven over the surface of the metal for a few minutes. Lastly, the fire is strongly urged, to drive off any remaining particles of antimony.

The alloy of gold and antimony may be fused with nitre. When this method is adopted, the alloy, with three times its weight of the salt, is placed in a crucible, covered with another reversed, and pierced in the bottom with a hole, which may be stopped with a plug of clay. It is to be gradually heated from above downwards, to avoid bubbling over. This is easily accomplished by leaving the furnace uncovered, using a charcoal fire, and kindling it from above. So long as any undecomposed nitre remains, a lighted coal, applied to the hole in the covering crucible, burns with great brilliancy, in consequence of the oxygen ascending from the decomposing salt. As soon as this evolution of gas ceases, the heat may be pushed without fear of spirting.

Galena, or sulphuret of lead may be substituted for antimony in the above-described operation. In this case, however, the metallic button contains silver as well as gold. The two metals in combination can be separated from the lead by cupellation.

Sulphur.—All these methods are based upon the greater affinity of sulphur for other metals than for gold. This metalloid can, therefore, be used alone, and is sometimes employed for this purpose. Gold is occasionally refined by melting it in a clay crucible, and, when in full fusion, throwing into it a few bits of sulphur as large as a pea. The crucible is well shaken and its contents poured into an ingot-mould.

Peroxide of manganese has been used to separate gold and

silver from the common metals. The alloy is either reduced to powder or finely laminated in a flatting-mill, and then fused with peroxide of manganese and bottle-glass. The foreign metals are oxidated and float up in the slag. The silver is found usually combined with the gold, though a portion of it is oxidized and diffused through the slag.

Many of the alloys of gold can be directly *cupelled*. That with lead is usually subjected to this operation. It is less difficult than the cupellation of silver, as gold does not have the same tendency to penetrate the cupel, nor does it volatilize nor vegetate like that metal. A higher heat can therefore be used without fear of loss, and indeed it improves the quality of the gold.

An alloy of gold and copper cannot be cupelled, in the large way, to any advantage, on account of the great quantity of lead necessary to carry off the copper, and the consequent consumption of time and fuel. According to Mitchell, fourteen parts of lead at least must be used in the alloy of gold coin, which contains 0.100 of copper. Besides, gold has so strong an affinity for copper, that, although the utmost caution has been observed, it still retains a portion of this metal after cupellation. The humid process is less objectionable.

The presence of platinum in an alloy greatly increases the difficulty of cupellation. This process cannot, indeed, be accomplished without the addition of silver, if that metal be not already present. The separation of the copper is effected with less waste of silver, by using a small quantity of lead and cupelling at a high temperature, than by employing more lead and a lower heat. The presence of platinum in an alloy of gold may be distinguished, according to Mitchell, by the following characters, independent of actual analysis: "If the assay be not heated very strongly, it does not pass, and the button becomes flat; this effect becomes very sensible, when the platinum is to the gold, in the proportion of 2 to 100. Under the same circumstances, the nitric acid solution proceeding from the parting, is colored straw yellow. At the moment an assay of an alloy containing platinum terminates, the motion is slower, and the colored bands are less numerous, more obscure, and remain a

much longer time than when there is no platinum; the button does not uncover, and the surface does not become as brilliant as that of an alloy of gold or silver, but it remains dull and tarnished. When the assay is well made, it is to be remarked that the edges of the button are thicker and more rounded than in ordinary assays, and it is of a dull white, approaching a little to the yellow; and, lastly, its surface is wholly, or in part, crystalline. These effects are sensible, even when the gold does not contain more than 0.01 of platinum. When the alloy contains more than ten parts of platinum to 90 of gold, the annealed cornet produced in the parting process, is of a pale yellow or tarnished silver color."*

Parting.—This is a term applied exclusively to the separation of gold from silver. There are two kinds, the *wet* and the *dry parting.*

Dry Parting.—This method is employed in the treatment of very poor alloys of gold, to concentrate it to a less proportion of silver, and to give a surface refining to certain alloys of gold and copper. The *concentrated parting*, as it was called, consisted in stratifying the laminated alloy with a cement varying in its composition. Some employed equal parts of sulphate of iron and common salt; others, 2 parts of sulphate of iron, 2 parts of sea salt, and 1 of chloride of ammonium, &c. Burnt clay or finely powdered brick, to the amount of three or four times the weight of the mixture, is added, and the whole made into a thick paste. The mixture is heated gradually to dull redness, and kept at that temperature for twenty-four hours, the alloy not being permitted to fuse. The rationale of this process is very simple. Sulphate of iron parts with its acid at a dull red heat The sulphuric acid, arising from this decomposition, attacks the base of the chloride, and the disengaged chlorine combines with the silver. The same mixture is sometimes used, with this difference, that nitre is substituted for salt and sal ammoniac. In this case, the liberated sulphuric acid unites with the potash of the nitre, setting free nitric acid, which acts to great advantage at this temperature, refining alloys which it would not touch in the wet way. Frequent fusions, laminations,

* Manual of Assaying.

and cementations are necessary in order to attain anything like purity.

The parting by sulphur is applicable to alloys containing a very small amount of gold, as small a quantity as $\frac{1}{3000}$ of gold being extracted from silver without loss.

To accomplish parting by this method, the alloy is first fused and granulated by being dropped into water, which is agitated by a rotary movement with a broom. This is mixed with sulphur, put into a crucible, and heated below the point of fusion to form sulphuret of silver by cementation. It is then heated to complete fusion, and poured into a conical iron mould, greased and heated. Should the mass be homogeneous, sulphuration is complete. It is then refused, with addition of more of the granulated alloy, or with a small quantity of iron filings. Sometimes the first fusion yields a button of suitable richness, and then the operation is complete. Should the button be very rich, gold remains in the sulphurated mass, and this must be fused as before with iron. Should the button contain excess of silver, it must be fused again with sulphur. The alloy is then to be roasted and cupelled with lead, and the mass of the sulphurets to be fused with iron to reduce the silver.

A modification of this process has been adopted, viz: to add litharge to the fused mass at the beginning of the operation. A button then subsides, containing the greater portion of the gold alloyed with silver. The rest of the gold is mixed with the sulphuretted slag. This is fused with litharge till all the gold is extracted from it. The buttons are fused again with sulphur.

Wet Parting.—This process may be conducted with nitric acid, sulphuric acid, or aqua regia.

A. *Nitric Acid.*—The best proportion of silver to gold, in an alloy which is to be acted upon by this acid, is two and a half of the former to one of the latter. Should the proportion of silver be less than this, it cannot be thoroughly dissolved out, because the gold envelops it in part, and protects it from the action of the solvent.* Should the silver greatly exceed three-

* Pettenkofer asserts that not more than $1\frac{3}{4}$ of silver to 1 of gold is necessary for the success of this process.

fourths of the alloy, the gold is obtained in such fine leaves and impalpable powder that some of it is infallibly lost in decantation, and even in the operation of boiling the acid liquid. It is necessary, therefore, to bring the alloy to the standard of somewhat less than three parts of silver to one of gold. Three parts of the former to one of the latter was the old formula, and, in consequence of this proportion, the operation necessary to accomplish this has been called *quartation*, an appellation sometimes erroneously applied to the whole process of nitric acid parting.

To perform this correctly, the mixed metals must be fused, and then poured into a cold ingot-mould, so as to mix them equally. A portion of the resulting alloy must be submitted to analysis, that we may ascertain the exact quantities of silver and gold present. This being determined, the alloy must again be melted with an additional quantity of one or the other metals, sufficient to bring it to the standard fineness. When the amount of alloy operated upon is not very large, it will be convenient to do this upon a cupel, with the addition of two parts of lead. This process can also be used on the large scale, though simple fusion, if the alloy is tolerably free from other metals, or fusion with pure nitre, if it is much contaminated, is commonly preferred.

The quartated alloy is now to be either granulated, by pouring it from the crucible into cold water, or, what is still better, if the quantity be small, flattened on an anvil, annealed, laminated in a mill, annealed again, rolled out to a very thin foil, and then made into a cornet or spiral, by winding it around a small cylinder. The cornet is now to be introduced into a suitable vessel, pure nitric acid is to be poured upon it, from time to time, and heat applied. When the silver is all dissolved, it is poured off, and the gold carefully washed by decantation. The washing is complete, when the water which comes off no longer communicates a cloudiness to a solution of common salt, after standing several hours.

The nitric acid must be poured on at different times, and of different degrees of strength. If concentrated acid be used from the beginning, the action will be so violent that some of

the gold will be lost by spirting. If weak acid be used throughout, all the silver will not be dissolved. The old method of treating the cornet was to pour thirty-five times the weight of the alloy, of nitric acid, at 20° (sp. gr. 1.15), and boil gently for fifteen to twenty minutes; then to decant the liquid, and replace it by twenty-four parts of acid (sp. gr. 1.26), boil for twelve minutes, decant and wash. Vauquelin, in his *Manuel de l'Essayeur*, recommends a somewhat different process. He boils on the cornet 72 parts of acid, at 22° Baumé (sp. gr. 1.16), for twenty-two minutes; he then decants and replaces it by from 60 to 100 parts of acid at 32° (sp. gr. 1.26), and boils for eight or ten minutes.

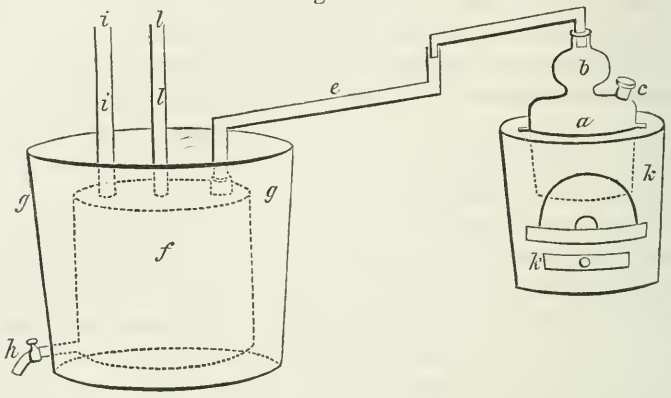
When a considerable quantity of copper remains in the alloy after fusion with nitre, or cupellation, this process is accurate. When, however, the alloy is finer, the gold always retains a little silver, so that a test alloy made of pure gold and silver, always yields a piece of gold, as separated by nitric acid, heavier than that originally introduced. This excess of silver is termed the *surcharge*, and usually amounts to two or three thousandths, though it sometimes exceeds this amount. M. Chaudet has suggested the following process, to get rid of it entirely. He cupels the gold, as already recommended, with three parts of silver and two of lead; makes a cornet; boils it with acid of 22° B., for three or four minutes; replaces this with acid of 32° B., and boils for ten minutes; decants again, and boils with fresh acid of 32° B. for eight or ten minutes longer. This leaves very pure gold.

The processes of liquid parting just described are mainly those of the assayer, who operates on small quantities of the precious metals. They are, however, applicable to larger operations by some slight modifications, and can be directly used by the refiner when working with small quantities of alloy.

When greater weights of these metals are to be purified, it is of importance to use such forms of apparatus as will avoid loss of the materials used in the parting, which on the large scale become very valuable of themselves. We give here a figure of an apparatus which may be used for obtaining the nitric acid originally, and for saving it after parting.

It consists of a platinum alembic or retort (*a*), with a capital (*b*), connected by a stoneware pipe (*e*), with a stoneware receiver (*f*), which is set in a refrigerating tub (*g*). The retort has a tubulure (*c*), furnished with a lid ground air-tight, which may

Fig. 51.



be kept in place by a weight. Through this, acid is introduced, and the process from time to time inspected. With the capital is connected a tube of platinum, which, at its other end, is united with the stoneware pipe (*e*). The receiver is furnished with an opening (*l l*), for inspecting the condensation of the acid, and a tubulure which receives the jointed pipe (*i i*), each joint entering conically into the one below. The upper joinings are not to be tightly luted, as the access of a little atmospheric air is desirable to oxidate the nitrous acid. Water is to be supplied in a gradual manner, and with a broad surface, by filling the upright pipes with quartz pebbles, so as partially to obstruct the tubes, and allowing a small stream of water to trickle over them so slowly as merely to keep them moist. The receiver is also furnished with a glass or stoneware stopcock (*h*) for drawing off the acid. A small air-furnace (*k*), furnished with an iron ring, on which the iron rim of the platinum retort rests, completes the apparatus. The refrigerating tub should be supplied with a constant stream of cold water from a lead pipe dipping nearly to its bottom, the hot water being allowed to escape over the edge of the tub.

The size of this apparatus will vary according to the purposes for which it is required. That described by Dr. Ure, from whose Dictionary the wood-cut has been copied with slight alterations, is estimated to part 100 pounds of alloy. Its capacity is ten gallons. The stoneware conducting-pipe (*e*) is at least 40 feet long, and the platinum tube, connecting it with the alembic, 2 feet long. The tubes (*i i*) and (*l l*) are 3 inches in diameter and 12 feet high. These dimensions are of course too costly for ordinary operations. The apparatus may be obtained at a very moderate cost, and in a much more compact form, by using a platinized retort, instead of one made of pure platina, and by making the connection with a Liebig's condenser, instead of the unwieldy stoneware pipe.

When the apparatus is used for making nitric acid, 100 parts of pure nitre or nitrate of soda (which is better on account of the greater facility of separating the resulting sulphate of soda from the retort and its higher value) is introduced into the alembic, the capital adapted, and the platinum tube luted to it. Through the tubulure *c*, 20 parts of strong sulphuric acid are poured, and the lid of the tubulure is closed. In an hour, 10 parts more of acid are poured in, and so in every hour till 60 parts are added. A few hours after the last addition of acid, and not till then, a little fire is made under the alembic. In 24 hours, if the heat has been properly managed, all the acid may be drawn off. Its final expulsion is aided by the introduction of boiling water in successive portions, the lid of the tubulure being closed after every aspersion.

The best strength of acid for parting is stated by Dr. Ure to be that of specific gravity 1.320. A measure, therefore, which will hold 16 ounces by weight of distilled water, will contain $21\frac{1}{3}$ ounces of this acid. It should be free from hydrochloric acid, and should not therefore be clouded by a few drops of a solution of nitrate of silver in distilled water after several hours' standing. Should any milkiness be produced by this reagent, the acid can be readily purified, by dropping into it a little silver in a state of minute division, before it is used for the operation of parting. Should this precaution be neglected, there will be an inevitable loss of gold, in direct proportion to the amount of

hydrochloric acid present, because that metal is soluble in a mixture of hydrochloric and nitric acids.

In making a chemical estimate of the necessary amount of acid, we find that it requires 38 parts of *aquafortis*, of specific gravity 1.320, to oxidate 100 parts of silver, and 111 more to dissolve it. But in actual working, we are compelled to use more of any given substance than a calculation based on its combining numbers would indicate, because towards the end of an operation the reactions, in consequence of the gradual saturation, become so feeble that too much time is taken up. Copper, it must also be borne in mind, consumes much more acid, both for oxidation and solution, so that it is advisable to supply silver freed from copper by a previous operation, and, if possible, containing a little gold.

The alloy, properly prepared, is then introduced into the alembic, the capital, and the joinings of the apparatus are made fast, and the upright tubes arranged as for the manufacture of nitric acid. For 60 parts of alloy 80 parts of acid are necessary. Ure prescribes for the composition of the alloy, two of silver to one of gold, though there certainly will be more gold in the surcharge, with an alloy of this proportion, than in such a one as has already been prescribed. The fire must be managed with caution, being moderate at first, and gradually increased as the parting advances. The excess of acid passes over and is condensed, and the nitrous acid fumes, arising from the decomposition of the aquafortis, are reconverted into nitric acid by the joint action of the atmospheric air and water contained in the condensing apparatus. In this manner, 20 or 30 parts of acid may be saved in a state of sufficient purity to be employed in a subsequent operation.

When the action of the acid on the alloy has ceased, which may be known by the cessation of the red fumes on opening the tubulure, the fire is extinguished, the alembic cooled and removed. Its liquid contents are then decanted into pure water, and the gold remaining in the retort boiled with some fresh nitric acid, to remove, as far as possible, the remaining silver. The heavy gold powder is now thoroughly washed with distilled or rain water, fused with nitre or borax, and cast into ingots.

The solution of nitrate of silver is now precipitated by clean plates of copper suspended in it, the completion of the operation being known by the absence of cloudiness on adding common salt or hydrochloric acid to a portion of the solution. The pasty precipitate of metallic silver is now to be thoroughly washed with soft water, dried by strong hydraulic pressure, fused, and cast into ingots.

The blue liquid, which is a solution of nitrate of copper, is now to be evaporated to dryness in the alembic, the tubulure *c* remaining open. When all the water is driven off, the lid is put on, the heat gradually raised, the apparatus remaining in the condition first described, and the nitric acid all distilled off, leaving black oxide of copper in the retort. This is a useful substance in the laboratory, and may be heated to redness, and put away in bottles with closely-fitting stopples. Or it may be used, if in large quantity, as an economical form for obtaining the sulphate of copper, 100 parts of it yielding 312½ of that salt in crystals.

The objections to this process have been already stated. The gold obtained by it always contains a little silver, and the silver retains a little gold. Many refiners, therefore, adopt another process, which is not liable to this objection, and which we now proceed to describe.

B. Sulphuric Acid.—The operation of parting with sulphuric acid was first suggested by M. Dizé, when he was inspector of the French mint. In the Parisian refineries, gold to the amount of one-tenth per cent. has been extracted from all the silver previously parted by the nitric acid process, and the operation has been found to be profitable.

The most suitable alloy for this process is one containing silver, 725; gold, 200; copper, 75. Alloys containing more gold are protected, to a certain extent, from the action of sulphuric acid; those which have more copper give a pasty alloy, from the formation of an anhydrous sulphate, which, being insoluble in concentrated sulphuric acid, prevents the action of the acid on the alloy. The alloy thus prepared is put in a platinum retort, and three times its weight of concentrated sulphuric acid is poured over it. The alembic is then covered with

its head, heat applied, and the operation goes on, the fumes of sulphurous acid being conducted away through pipes, which, in some factories, open into the chimney, so that the vapors are carried off. This acid may be saved by reconverting it into sulphuric acid, by means of nitrous acid fumes, and a condensing apparatus; or it may be directly made use of by conducting it over a magma of lime, as in the gas-houses, to form the sulphite of that base. The production of this sulphurous acid is due to the deoxidation of the oil of vitriol, one atom of its oxygen combining with an atom of silver, while the resulting oxide combines with the sulphuric acid present, to be converted into sulphate of silver. The solution goes on vigorously with a copious evolution of sulphurous acid for the first three or four hours, but afterwards more slowly, and the operation is not completed till about twelve hours more have elapsed.

When the solution is complete, that is to say, when all the silver has been converted into a sulphate, the entire contents of the alembic are emptied into water, which must be in sufficient quantity to bring the liquid to 50° or 20° B. This dissolves the crystalline sulphate of silver which had sunk to the bottom of the alembic during the operation, and the only insoluble matter which remains, if the operation has been properly conducted, is the heavy pulverulent gold which subsides. The liquid is now decanted, the gold repeatedly and thoroughly washed, the washings being of course emptied into the same vessel with the decanted sulphate. The silver is precipitated and treated as already described under the head of Nitric Acid Parting. The gold is fused with a little nitre, to get rid of any copper which may have escaped the acid, and the melted metal poured into an ingot-mould.

It may be remarked here that, in concentrated solutions, the precipitation of the silver takes place very slowly, and that solutions of sulphate of copper which have a specific gravity higher than 1.19 will oxidate the silver. The solutions of sulphate of copper are evaporated, crystallized, and recrystallized. The acid mother waters are evaporated to sp. gr. 1.56, 55° Baumé; some anhydrous sulphate of copper precipitates, and the supernatant acid liquid is pure enough to be used in subsequent operations.

The boilers in which the silver is precipitated becomes gradually coated with metal, which, when scraped off, washed, and fused with nitre, yields pure silver.

This process will separate from silver less than the two-thousandth part of gold.* The general rule of the French refiners is to retain the copper and the gold and return the silver, when the alloy contains less than a thousandth of gold. When above this standard, the prices vary with the nature of the alloy, averaging, however, about fifty cents to the pound troy.

The process just described is not applicable to the refining of gold bullion or any mixture of gold and silver containing lead or tin. Independently of the fact that lead forms an insoluble salt with sulphuric acid, which would mix with and contaminate the gold, the presence either of this metal or of tin, in company with the acid liquor in the platinum alembic, would destroy the precious vessel in a very short time. These metals are therefore got rid of at the beginning by fusion with nitre, if their proportion be small, or by cupellation, if they exist in large quantity.†

* Pettenkofer's experiments on this process, as quoted by Booth and Morfit, in their report to the Smithsonian Institution, on the progress of the chemical arts, are deserving of attention. They were performed at the refinery in Munich on kronenthaler (crown-dollars), which contain $\frac{7}{900}$ of gold. The parting is rapid, till the alloy reaches the fineness of 958 to 960 thousandths; after which, long-continued boiling, with great excess of acid, raises it to only 970, 28 of the remaining parts being silver, and 2 platinum. No excess of acid, even with repeated boiling, will raise the standard more than one-fourth of a thousandth above this. A second fusion and parting becomes necessary. He thinks the silver is alloyed in the metallic state with the gold, but that it does not exist in its normal condition. Sulphur may be distilled over it, but it gives no trace of sulphuret of silver. When heated with boiling sulphuric acid mixed with bichromate of potash, gold is dissolved and sesquioxide of chrome is formed; but neither silver nor platinum is attacked. The silver may be extracted by fusion with bisulphate of soda or potassa. The great preponderance of gold seems to assimilate the alloyed silver to itself, just as silver renders platinum soluble in nitric acid, or platinum causes gold to be corroded when fused with nitre.

† For a fuller description of the French establishments for parting, and the processes there adopted, see Ure's Dictionary of Arts and Manufactures and Mines, article "Refining of Gold and Silver."

C. Aqua Regia.—The separation of gold and silver is very conveniently made by this agent, when the amount acted upon is small and contains but little silver in proportion to the gold. It is not suitable for large operations, as the acids used are necessarily lost. The process is founded upon the solubility of gold in nitro-hydrochloric acid, and the insoluble character of chloride of silver.

This process has the advantage of requiring no preliminary preparation of the alloys. All that is necessary for its success is, that the gold should predominate considerably over the silver. Should there be an excess of silver, the chloride which forms will protect the gold from the action of the acid. This difficulty can indeed be overcome by washing off the acid, dissolving the chloride of silver in ammonia, laminating the alloy, and reapplying the solvent; but this operation is tedious and troublesome, so that when silver is present in excess, it is much better to adopt one of the former methods of parting.

The solvent is prepared usually by mixing from one to two parts of nitric acid of 32° B. (sp. gr. 1.28), with four parts hydrochloric acid of 22° B. (1.178.) The laminated or granulated alloy is introduced into this and digested at a gentle heat till all fumes cease to pass over. At first, the fumes are red and heavy, consisting of nitrous acid, but towards the close of the operation they become yellowish or greenish, and finally, if the heat is urged, they are white. At this period, the action of the acid has ceased. The liquid is then poured off, a fresh supply of acid poured on, boiled for a short time, and then decanted. The remaining chloride of silver is then washed and reduced by fusion with carbonate of potash, or by reduction with metallic zinc or iron in the humid way. The gold is then to be precipitated with the protosulphate of iron, if there are any other metals present; if only silver was in the alloy, oxalic acid may be used as a precipitant.

Simple as this operation appears, some precautions are necessary in order to insure success. Great care must be taken to rid the solution of any excess of nitric acid, otherwise the precipitation with sulphate of iron will be difficult, the gold being redissolved as fast as it is precipitated. This is effected by

evaporation to dryness, repeated several times, with the addition of hydrochloric acid. The evaporation must be conducted over the water-bath; for, should the heat be raised above 212° F., the terchloride of gold will be reduced to metallic gold and the protochloride. Nitric acid being completely expelled, the protosulphate of iron is added, and the solution is allowed to stand for twenty-four hours. It is better to have the precipitating jar well covered, or to add excess of hydrochloric acid, to dissolve the peroxide of iron as fast as it is formed. When the precipitation is ended, the liquid is decanted, and the gold thoroughly washed, first with hydrochloric acid, then with acidulated water, and then with pure water. The gold is then fused with nitre and borax, and cast in an ingot-mould. Precipitation of gold by copperas is a slow process. I have sometimes obtained the metal sufficiently pure for all practical purposes, in a much more rapid manner by thoroughly drying the chloride, subjecting it to a temperature of about 300° F. and then fusing it with nitre.

When platinum is present, the process of parting must be modified. Advantage must be taken of the property possessed by this metal of becoming soluble in nitric acid when alloyed with silver. If there should be copper present, this should be removed by cupellation, the necessary amount of silver added, and the resulting alloy granulated and boiled with nitric acid.

The standard of the alloy of gold is expressed, in mercantile phraseology, by *carats*. This term is said to be derived from *kuara*, the name of a sort of bean, the fruit of a species of *erythina*, in the province of Shangallas, in Africa. This name signifies, in the jargon of the natives, the sun, the tree which bears this bean producing flowers and fruit of a brilliant flame color. The pods of this plant, being nearly uniform in their weight, have long been used by the natives in weighing gold-dust, which is sold in large quantity in this province. From Africa, say the etymologists, from whom we take this account, the beans were exported to India, where they were used for weighing diamonds. The diamond carat, however, differs in weight from the gold carat. The former weighs four nominal grains, each of which is equivalent to .989 grain troy. The gold carat, on the other hand, which is also applied to expressing the purity of al-

loyed silver, is usually a mere proportional weight, having no definite value. Sometimes, however, a definite weight is spoken of when the term carat is used, and then it means 12 grains. When the proportional carats are used, the entire mass is supposed to be divided into 24 parts, each of which is a carat. When great exactness of expression is required, these carats are each divided into 32 parts, so that the entire mass is divided into 768 32nds. Absolutely pure gold, of course, has the whole weight of the mass without alloy, and is therefore said to be 24 carats fine, or simply fine. Should the mass contain one part of silver or other metal, it will be called 23 carats fine. The mercantile expression for the fineness of gold, therefore, simply indicates the number of twenty-fourths of the entire mass, which consist of the pure metal. A more scientific method, however, of rating these is to express the proportion of the precious metal in thousandths. Thus, when we say that standard American gold has the fineness of 900 thousandths, we mean that, in every thousand grains of the coin there are 900 grains of pure gold, the remainder being a variable mixture of silver and copper, generally, however, in the proportion of 25 to 75.

GOLDBEATING.

The art of reducing gold to fine leaves has been practised from a very remote antiquity. The Romans were in the habit of using it in ornamenting their houses, and Pliny says that it was hammered out so as to cover a space 600 times greater than the original surface cast. Modern workmen have carried the lamination of gold more than one thousand times farther than this.

It is generally supposed that it is essential that the gold employed in this art should be absolutely pure. This, however, is a mistake. In fact, there is very little goldleaf to be found which possesses this perfect purity, and many workmen believe that the malleability of the metal is increased by the admixture of alloy. The introduction of a little copper or silver certainly increases the tenacity of the leaf, and prevents the fine laminæ from adhering to one another, a property possessed by the pure

metal in a remarkable degree, and one which is very troublesome to the goldbeater. There are two varieties of goldleaf, the pale and the deep colored. The former is alloyed with silver alone, the latter with silver and copper. Tints between these can be obtained by careful management of the alloy.

The gold is melted with nitre, or borax, or both, in a crucible, and cast into ingots, the size of which varies according to the mode of working adopted by different manufacturers. They are flat and oblong, so as to be of convenient form for lamination. The French goldbeaters forge this ingot, annealing it from time to time, as they find it becoming hard and disposed to crack. The ingots, or portions of them, of suitable size, are now passed through a laminating machine, consisting of two very fine, hard, polished steel rollers, with the necessary apparatus for adjusting the distance between them. The width of the metallic strip remains unaltered, and the flatting is carried on entirely at the expense of its longitudinal diameter, so that it is at last reduced to a long ribbon not more than $\frac{1}{1800}$ of an inch in thickness. This ribbon is now annealed in the fire, and then cut up in pieces of about an inch square, which are introduced into a packet made of leaves of fine vellum, or of prepared animalized paper, so that the metal and the vellum alternate. This packet is enveloped in a strong parchment case, and is then ready for the operation of beating.

The beating is performed with a hammer, of about sixteen pounds' weight, on a solid smooth block of marble, strongly framed, and surrounded by a raised wooden ledge, and having a leathern apron in front to catch any scattered fragments of the precious metal. The hammer is short-handled, and is worked with one hand. The elasticity of the packet causes the hammer to rebound, and saves labor, by obviating the necessity of lifting so great a weight. Every now and then, in the interval between two blows, the packet is turned, so as to be equally beaten on both sides. The blow is struck directly in the middle of the packet, and the hammer is slightly convex, that it may compress the gold most in the centre and dispose it equally on either side. The workman withdraws the packet from time to time to cool it, as the heat developed by these continual heavy blows would in-

jure the skin; and he works it backward and forward to overcome any adhesions between the gold and the vellum. At intervals the packet is opened, to see that everything is going on satisfactorily, and the leaves are occasionally shifted, that all may be uniformly compressed. The beating is continued till the leaves have reached the edge of the packet, or till the one inch squares cover each a space of four inches square.

The result of this first beating is gold foil, which is cut evenly and put into books, weighed and numbered. The numbers run from 4 to 36, and indicate the number of grains which each leaf weighs.

Should the beating go on to the manufacture of leaf, these products of the first beating are taken out, laid on a leathern cushion, and cut each into four parts with a knife. Each of these parts is introduced into another packet of goldbeater's-skin or prepared ox-gut, and beaten in the same manner as before with a hammer weighing from ten to twelve pounds, till they expand to the size of the packet.

After this second beating, the leaves are again removed and quartered by a piece of sharp-edged cane, as they have a tendency to adhere to a steel knife. They are replaced in a packet as before, and again beaten out nearly to its diameter. The gold has now reached such an attenuation that 100 square feet of it will only weigh an ounce. It can be beaten out thinner even than this, and an ounce made to cover 160 square feet, but the process is tedious and wasteful from the number of broken leaves, and attended by no corresponding advantage.

The thin leaves are now taken out of the packets with wooden pliers, and, by means of the breath, blown flat on a cushion, an operation requiring the dexterity of long practice. The broken leaves are rejected, and the rest are cut to a uniform size with a sharp cane, which reduces them to 3 or $3\frac{1}{2}$ inches square. They are then transferred to little books, the leaves of which have been covered with red chalk, to prevent the metal from adhering. Each book usually contains 25 leaves of gold. The average thickness of ordinary goldleaf is $\frac{1}{282000}$ of an inch.

ALLOYS AND NON-SALINE COMPOUNDS.

Gold.—Gold varies in its appearance, in accordance with the method by which it has been obtained. The precipitate by protosulphate of iron is a dark-brown powder; that by oxalic acid has a yellower tint, and here and there a metallic lustre; while the gold obtained by evaporating the terchloride at 300° is in spongy masses of a dull yellow tint, resembling, in some degree, what is known to artisans as *deadened gold*, though even less lustrous than that. The metal obtained by *parting* has a loose spongy texture, and a reddish tint. By annealing in a muffle below the point of fusion, this dull tint leaves it; it contracts greatly and assumes a yellow metallic lustre. In all these states gold is capable of being welded by simple pressure.

A substance has recently been prepared for the use of dentists, under the title of crystallized or sponge gold. The first term is inappropriate, as there is often nothing of the crystalline character about it. The material presents very different appearances. That imported from Europe is in small porous masses of a dull yellow or reddish-yellow tint. Again, it is found in small ovoid lumps, also porous, but tolerably resistant, though readily welding under pressure. A third variety is in cakes made of fine filaments of lustrous gold. This form has a greater tenacity than either of the preceding varieties.

The preparation of this article has been kept profoundly secret. I have experimented upon it, and succeeded in imitating it. A preparation, much resembling it, may be made by simply annealing the gold obtained from alloy by the process of parting. It may also be imitated by decomposing the dry terchloride at a high temperature, and then annealing the resulting cake at a dull red heat. The gold from which mercury has been distilled, after the process of amalgamation, also resembles the sponge gold.* In all these preparations, it is, of course, necessary to be absolutely certain of the purity of the metal.

* Since the above was written, the author has seen the formula of the New York patentee.

He amalgamates the gold with from 4 to 12 times its weight of mercury, triturates, heats to about 180° F., and allows it to stand for several hours.

Solid gold, whether molten or welded, is universally known by its brilliant yellow color. It is capable of receiving a very high lustre, but is inferior in brilliancy to steel, silver, and mercury. When pure, it is so soft that it cannot be made up into jewellery or other articles to any advantage. It tarnishes readily, because it is so easily scratched, and wears away rapidly for the same reason. In ductility and malleability, it excels all other metals. A single grain may be drawn into a wire 500 feet long, or hammered into leaves of more than 50 square inches in superficial extent, and one three hundred thousandth of an inch in thickness. The specific gravity of gold varies. The molten metal has a density of 19.26, while the hammered ranges from 19.4 to 19.65. Gold fuses at 2016°, according to Daniell, with considerable expansion, and on cooling contracts more than any other metal.

Gold has a very feeble affinity for oxygen. No length of exposure, no amount of heat is sufficient to force it to combine with oxygen. When ignited in oxygen gas, or by a current of electricity, or by the oxyhydrogen blowpipe, it is dissipated in the form of a purple powder, which has been supposed by some to be an oxide, though others will have it to be nothing but finely divided gold. The last opinion is rendered probable by the fact that the presence of oxygen is not necessary for the production of this so-called purple oxide, it being produced by ignition in an atmosphere of hydrogen.

Not only is gold difficult to oxidate, but it is also scarcely possible to volatilize it. The heat of a blast furnace only fuses it, without loss of weight, and it is only with great difficulty that it is dissipated in the powerful heat of the oxyhydrogen blowpipe.

It is insoluble in the simple acids, no matter how concentrated they may be. Of the metalloids, it is readily soluble in chlorine and fluorine. *Aqua regia*, or nitro-hydrochloric acid, readily dissolves it. This action is in all probability due to chlorine, a mixture of nitric and hydrochloric acids being a constant source of that gas, so long as they mutually decompose each other.

He then treats it with nitric acid, in the manner already described under the head of parting gold and silver. Finally, he anneals the residual gold at a heat just short of the fusing-point of gold.

Nitrofluoric acid is also a solvent of gold, fluorine, in like manner, being the active ingredient.

The symbol of gold is Au, its combining number 199.207 on the hydrogen, and 1243.613 on the oxygen scale. Berzelius regards it as Au_2; its combining number, on this hypothesis, would, therefore, be 99.604 on the hydrogen scale.

Protoxide of Gold.—AuO. 207.22. When the peroxide or perchloride of gold is boiled with a solution of caustic or carbonated fixed alkalies, or when the terchloride is precipitated by dinitrate of mercury, there remains a dark-green or violet powder, which does not combine with acids, and which is resolved by hydrochloric acid into terchloride and metallic gold. It is most conveniently obtained by treating protochloride of gold with a cold solution of caustic potash. In consequence of a series of decompositions, chloride of potassium makes its appearance in the solution, and the oxygen of the potash is transferred to the gold. The oxide thus obtained is of an olive-green color, partially soluble in the alkaline solution, and spontaneously decomposable, being resolved into terchloride and metallic gold.

Peroxide of Gold.—AuO_3, 223.24. This is also known as teroxide of gold and auric acid. It may be obtained by digesting the terchloride with a slight excess of magnesia or oxide of zinc, which throws down nearly all the gold with magnesia or zinc. The precipitate is washed with water and digested with strong nitric acid, which dissolves the magnesia or zinc, together with some gold, leaving a brown anhydrous oxide. Digestion with dilute nitric acid furnishes a reddish hydrated oxide. Another method of preparing it, is to dissolve one part of gold in the usual way, to render it quite neutral by evaporation, and redissolve in twelve parts of water. One part of carbonate of potassa, dissolved in twice its weight of water, is then added, and the whole digested at about 170°. Carbonic acid escapes and the hydrated peroxide subsides as a brownish-red precipitate. It is now thoroughly washed, dissolved in pure nitric acid of specific gravity 1.4, and the solution decomposed by water. The hydrated peroxide is thus obtained in a state of purity, and is rendered anhydrous by a temperature of 212°.

This oxide is yellow when hydrated, and black when anhy-

drous. It retains its oxygen with a very feeble attraction, so that it may be decomposed at a heat below redness. Indeed, it is spontaneously reduced, though not completely, when kept in the dark, and loses all its oxygen on exposure to sunlight. Hydrochloric acid dissolves it readily, forming the common solution of gold. Nitric and sulphuric acids also dissolve, but seem to form no definite compound with it, as it is easily precipitated from these solutions by the addition of water.

According to the experiments of Pelletier, this oxide behaves very differently towards the alkalies. In solutions of potassa and baryta it is dissolved, apparently forming regular salts, in which the oxide plays the part of a weak acid. This chemist, therefore, denied that the teroxide of gold is a salifiable base, and transferred it to the acids, under the title of auric acid, its salts being called aurates.

When the teroxide is kept in a strong solution of ammonia for a day, fulminating gold of a deep olive color is generated. A similar compound is obtained by precipitating the terchloride of gold with ammonia, and digesting the resulting precipitate with the precipitant in excess. The precipitate is a bright opaque gold yellow, and consists of fulminating gold with double chloride of ammonium and the metal. This compound may be dried at 212°; but friction or a heat of 290° immediately produces an explosion. It is best made in small quantities and dried in the open air.

The results of the detonation are metallic gold, water, nitrogen, and ammonia. Dumas's analyses indicated its composition to be one equivalent of gold, six of hydrogen, two of nitrogen, and three of oxygen, or $Au,N_2H_6O_3$. He expressed its composition by the formula $AuN,+H_3N+3HO$; that is, he regarded it as a hydrated nitruret of gold with ammonia. Turner considers it to be a diaurate of ammonia, and expresses it by the formula $2NH_3AuO_3$.

Purple Oxide.—It has already been said that there were grave doubts of the propriety of the term oxide applied to this substance. This question will be discussed more at large under the next head, Purple of Cassius. In favor of the opinion that the so-called purple oxide is only metallic gold in a state of fine

subdivision, it may be urged that every tyro in chemistry knows that, when a precipitant of metallic gold is added to very dilute solutions of this metal, its first effect is to communicate a bright purple tint to the whole fluid. Besides, the heat to which this substance is subjected in the glass-stainer's establishment, ought to discharge any combined oxygen. Berzelius, however, advocated the opinion that there is an intermediate oxide between the protoxide and the teroxide, founding his arguments upon the analogies of the oxides of silver.

Purple of Cassius.—This unintelligible preparation of gold is much employed by the porcelain manufacturer, the manufacturer of colored glass, and the dentist, to give various tints of red and pink to their wares. The preparation of this exquisite pigment is a matter of great nicety, and sometimes the most experienced manufacturers are disappointed in their results.

When, into a weak solution of terchloride of gold, protochloride of tin, acidulated with a few drops of nitric acid, is let fall, a purple tint is communicated to the entire solution. With care a precipitate may be obtained. It must be observed, however, that success depends entirely upon hitting the exact condition of the tin and the gold. The chloride of the latter must be neutral and free from nitric acid; that of the former must be a due mixture of the perchloride and the protochloride. The protochloride of tin alone is a powerful deoxidating reagent, and throws down a brown precipitate of gold-tin; the perchloride affords no precipitate whatever; but a neutral solution, of one part crystallized protochloride of tin, with two parts crystallized perchloride of tin, throws down from a solution of one part crystallized terchloride of gold, the purple precipitate required. According to Fuchs, a solution of the sesquixode of tin in hydrochloric acid, or of the sesquichloride in water, which is the same thing, accomplishes the same result when dropped in a properly dilute solution of gold.

As this is an important article to the dentist, several different formulæ for obtaining it are here inserted.

Fuchs recommends manufacturers to add to a solution of sesquichloride of iron a solution of protochloride of tin till the iquid assumes a pale-green tint. The reaction here consists in

the abstraction, from the sesquichloride of iron, half an atom of chlorine, which unites with the chlorine of the tin salt, converting that compound into a sesquichloride, while the iron is left in the state of protochloride, which is a pale sea-green salt. Add to the solution thus obtained a properly dilute solution of terchloride of gold which has been freed from nitric acid. A very fine precipitate of purple of Cassius falls, and the protochloride of iron remains in solution. The purple thus prepared is said to keep a long time in the air without alteration. Mercury does not abstract from it the smallest particle of gold.

Berzelius dissolved gold in aqua regia, expelled all the nitric acid in the manner already described, and then diluted largely with water. He ascertained the proper point of dilution by dipping a glass rod in a solution of sesquichloride of tin, and then into the gold solution, and adding water till the precipitate redissolved by agitation. He then added a solution of sesquichloride of tin portion-wise, stirring the liquid after each addition, till the chloride of gold was all decomposed. The brown or purple liquid then deposited the purple after standing for twenty-four hours. Care must be taken, in following this method, not to add an excess of the tin salt.

Buisson's formula is as follows: Dissolve 1 gramme* of the best tin in a sufficient quantity of hydrochloric acid to make a neutral solution. Dissolve 2 grammes of tin in aqua regia, composed of 3 parts nitric to 1 part hydrochloric acid, and warm it, that no protochloride may remain in solution. Then dissolve 7 grammes of pure gold in aqua regia, composed of 1 part nitric and 6 parts hydrochloric acid, taking care to make the solution neutral. Dilute the last solution with $3\frac{1}{2}$ litres (about 3 quarts) of water, and add to it the perchloride of tin, and after that the protochloride, drop by drop, till the precipitate assumes the desired color. Wash the precipitate as quickly as possible.

Another formula requires the operator to warm 10 parts of perchloride of tin and ammonium with 1.07 parts of tin and 40 of water, till the tin is all dissolved; then add 140 parts of water, and add it to a solution of 1.34 parts of gold in aqua

* A gramme is 15.434 grains.

regia, diluted with 48 parts of water, as long as a precipitate falls. Wash and dry the resulting purple at a temperature of 212°.

The French Pharmacopœia orders 10 parts of chloride of gold to be dissolved in 2,000 parts of distilled water. To this is to be gradually added, as long as a precipitate falls, a solution of 10 parts of pure tin in 20 of hydrochloric acid. The precipitate, after subsidence, is washed by decantation, filtered and dried at a very gentle heat.

The same substance is more easily obtained by fusing together 150 parts of silver, 20 of gold, and 35.1 of tin, and dissolving out the first-named metal with nitric acid. In order to avoid loss of tin by oxidation, it is best to granulate the three metals, and then to throw them into a redhot black-lead crucible containing a little borax.

Frick's prescription is: Let tin be digested in very dilute aqua regia without heat, till the fluid becomes faintly opalescent, when the metal must be taken out and weighed. The liquor is to be diluted largely with water, and a definite weight of a dilute solution of gold, and dilute sulphuric acid, are to be simultaneously stirred into the nitro-muriate of tin. The solutions must be so managed that the gold in the one shall be to the tin in the other in the proportion of 36 to 10.

The description of the methods of obtaining this substance have been thus minutely given, because it is an invaluable material to the manufacturer of incorruptible teeth. The common name by which it is known to him is gum-color.

The precipitate when recently made is a brownish-purple or deep violet color, soluble in water of ammonia, with a deep purple color, from which it is precipitated by acids or heat. The color is usually changed by this precipitation, and assumes more of a blue tint. When the ammoniacal solution is heated to 140° or 176°, in a close flask, it deposits purple rapidly without redissolving it; on evaporation, the precipitate is found to have changed its character, though its appearance is the same. It is now insoluble in ammonia. The solution gradually decomposes in the light, depositing metallic gold. The purple precipitate becomes brighter when dry, but still has a brownish tint,

resembling, more nearly than anything else, a dirty and faded episcopal purple.

The chemical nature of this remarkable compound still remains a problem. According to Berzelius, its sole loss when heated to redness is 7.65 per cent. of water, and the residue has a brick-red tint, arising, it has been supposed, from a mixture of metallic gold and binoxide of tin. Fusion with nitre converts it into stannate of potassa and an alloy of gold and tin. Nitro-hydrochloric acid dissolves out the gold and some of the tin, leaving peroxide of tin. The action of mercury is variously stated. Some chemists say it has no effect upon the compound, and others that, at a temperature of from 212° to 300° F., it dissolves out all the gold. Fuchs's precipitate loses no gold on the addition of mercury.

The proportions of the different ingredients are variously stated by different authors. The following table will give an idea of these variations:—

	Gold.	Oxide of tin.
Oberkampf, purple precipitate .	39.82	60.18
" violet " .	20.58	79.42
Berzelius	30.725	69.275
Buisson	30.19	69.81
Gay Lussac	30.89	69.11
Fuchs	17.87	82.13

The opinions entertained by different chemists of the actual constitution of this precipitate differ still more widely. Thus it has been called a terstannate of the protoxide ($AuO,3SnO_2+4HO$) with 42.5 per cent. of gold; a hexa-stannate of the protoxide ($AuO,6SnO_2\times 6HO$) with 28 per cent. of gold; a protostannate of tin and gold ($SnO,3SnO_2+AuO,2SnO_2+6HO$); a stannite of the deutoxide of gold (purple oxide) $AuO_2,2Sn_2O_3+4HO$) with 39 per cent. of gold, and this is the view of its composition adopted by Berzelius; or, finally, a sesquixode of tin and stannate of the deutoxide of gold ($2\ (SnO,SnO_2)+AuO_2,2SnO_2+6HO$) with 28 per cent. of gold.

It is manifest that the purple precipitate of Cassius cannot be a mere mechanical admixture of its ingredients, because its color is changed in a manner that mere admixture could never

effect; and, farther, because it is soluble in ammonia. It has been argued that, as mercury extracts nothing from the carefully made purple, the gold must be oxidated; and that, as the precipitate is thrown down from the terchloride of gold by the protochloride of tin, and not at all by the perchloride of this metal, it must be in a low state of oxidation; and, farther, that, as a stannate of the protoxide would probably lose oxygen, when heated, which the purple does not, it is most probably either a stannate or a stannite of the purple oxide.

This precipitate, when fused with vitreous substances, such as flint-glass, or sand and borax, yields a purple enamel, which is used for giving a purple or pale-red tint to porcelain and glass. The depth of the tint depends very much upon the management of the frit, as will be hereafter explained. It has been supposed to be a compound of the purple oxide of gold with the earthy matters of the flux.

Protosulphuret of Gold.—AuS. 215.3. When sulphuretted hydrogen is passed through a boiling solution of terchloride of gold a dark powder subsides, containing one atom of sulphur in combination with one atom of gold. It is black, with a dark-brown streak, and contains 92.5 per cent. of metal.

Tersulphuret of Gold.—AuS_3. 247.5. Sulphuretted hydrogen passed in a stream through a cold solution of the terchloride, throws down a black tersulphuret of gold. When formed by precipitating the sulphauride of potassium with acids, it is yellow. Both sulphurets are decomposed by heat, the sulphur being driven off, and metallic gold left. The persulphuret dissolves readily in sulphuret of potassium, and acts as a sulph-acid to the other positive sulphurets, and as a sulpho-base to the negative sulphurets of arsenic, molybdenum, &c. The *sulpho-carbonate*, AuS_3, $3CS_3$, is a black precipitate formed by bringing together the solutions of the terchloride of gold and the sulphuret of carbon.

Phosphuret of gold is a whitish metallic compound, more fusible and more brittle than gold. It is made by direct combination or by heating gold with phosphoric glass and charcoal. When heated in the air, phosphorus burns off.

ALLOYS OF GOLD.

Gold readily combines with most of the metals, forming alloys of various colors, and various degrees of hardness, toughness, and malleability. Pure gold, as has already been said, is too soft for the purposes of the workman in this precious metal. The principal base metal used to alloy it, is copper.

Of the alloys with the rarer metals, it is not necessary to say much in this place. It is well enough, however, to advert to those with *arsenic* and *antimony*, because these are contaminations which may very readily find their way into the gold prepared by the dentist for his plate-work, or into that which he obtains from the jeweller's scraps and the sweepings of his own room.

Arsenic, even in vapor, forms a gray, brittle alloy with gold, containing $\frac{1}{241}$ of arsenic, which cannot be wholly expelled by two hours' fusion in an open crucible. Arsenic in the proportion of $\frac{1}{900}$ renders gold brittle without changing its color. The alloy with $\frac{1}{9}$ of *antimony* is pale and brittle, and gives up its antimony by heat; and $\frac{1}{1920}$ of antimony is sufficient to destroy the malleability of gold.

The alloys with the *platinoid* metals are brittle and pale, unless the gold is in considerable excess. With *palladium*, gold forms a hard pale alloy, 6 parts of gold to 1 of palladium being nearly white. The gold ores of Gongo Seco, in Brazil, contain this substance in sufficient quantity for separation on the large scale. *Iridium* is said to form a yellow ductile alloy with gold, probably through the agency of copper, with which it forms a fusible and malleable alloy. Pure iridium is the most refractory of all metals, Berzelius having failed to fuse it, and Mildren having succeeded with difficulty, by the use of his powerful batter . Bunsen and Hare have also fused it. Iridium is sometimes found in combination with the scraps of native gold from alluvial washings. Its sharp, hard crystals are infusible at any working temperature, so that they must be picked out carefully before the gold is melted, or they will render it impossible to work the softer metal.

It must be borne in mind, however, that in this manner only the coarse particles are removed. There remain finer crystals,

which are very troublesome. In California gold, this substance is occasionally very annoying to those who fuse it directly, and sometimes, from the extreme hardness of the crystals, materially injures the rolls used in milling out plate-work. It is necessary, therefore, to resort to the operation of parting. The iridosmin of California contains the new metal ruthenium.

The alloy, with *platinum*, renders gold pale, but does not diminish its malleability, unless it forms a large proportion of the alloy. When united with silver it may, as has already been said, under the head of parting, be dissolved out with nitric acid.* *Rhodium* forms malleable alloys with gold. In Mexico, it has been found alloying the native gold in considerable quantity, averaging 31 per cent. of the compound.

Lead and *bismuth* are alike destructive to the malleability of gold. An alloy composed of only one part of either of these metals and 1,920 parts of gold is brittle. The mode of separation has already been pointed out under the head of metallurgic treatment of alloys.

Zinc hardens gold, as well as whitens it, and enters as an ingredient in various compounds made by the goldsmith. Eleven parts of gold to one of zinc make an alloy, pale, greenish-yellow, and brittle. Equal parts of gold and zinc produce a white, hard metal. One part of brass to one of gold gives a brittle alloy. *Tin* is very injurious to the malleability of gold. Sulphuret of antimony removes these metals. *Iron* does not so seriously interfere with the working of gold. One part of the latter metal combined with eleven of gold produces a malleable alloy. Of the alloys of gold with *mercury* nothing need be here added to what has already been said.

Silver unites with gold in every proportion, the color being nearly proportional to the amount of the paler metal introduced. The alloy is harder and more fusible than gold, the hardest consisting of 2 parts of gold to 1 of silver.

* This metal is combined with gold much more generally than is usually supposed. Its presence confers upon the gold the property of solubility in nitre on fusion. When gold is purified by nitre, the slags are not entirely dissolved in water, but there remains a fine grayish sediment, composed of alumina, silica, potassa, oxides of iron, copper, lead, platinum, gold, and metallic gold.

Copper is the most valuable of the metals for alloying gold, as it is retained with greater firmness, and communicates, when properly managed, the requisite degree of hardness, without injuring the malleability of the gold. The only perceptible effect it has is to redden the alloy, a result which may be avoided by adding silver, or by treating the finished work with caustic ammonia. It must be borne in mind, however, that an alloy of gold with copper about 19 carats fine, or, to speak more correctly, containing 76 parts of gold to 24 of copper, is crystalline in its texture, and brittle. This is a definite compound and may be represented by the formula $AuCu_2$. The addition of either metal to this alloy diminishes its brittleness.

The common alloy of coin is 90 gold to 10 copper. The yellow coin of the United States is composed of 90 parts of gold, $2\frac{1}{2}$ of silver, and $7\frac{1}{2}$ of copper. The redder coins have less silver. Medals usually contain more gold, being less subjected to abrasion than coins. Their proportions are 91.6 of gold to 8.4 copper. The common alloy for jewelry is 75 of gold to 25 of copper, zinc or silver being occasionally used to take off the red tint given by the copper. The proportions recommended by Dr. Harris for plate-work, are, for plate for the upper jaw, gold 20, copper 3, silver 1; for plate for lower jaw, gold 21, copper 2, silver 1; for springs, gold 18, copper 5, silver 6.

Some little care is needed in the preparation of these alloys. Owing to the difference in the specific gravity of the metals, they are liable to separate from one another after fusion. Silver, especially, parts from gold in this way. To obviate this, it is necessary to cast the alloy in shallow ingots, and should it, notwithstanding this precaution, be unequally mixed, it must be cut up and melted over again, when it will be more uniform. Sometimes repeated fusions are necessary; generally, however, two will suffice. It is commonly recommended to add borax to the fusing mass. This has a tendency to cover the metallic bath, and give a smooth bright surface to the metal. But it is impossible to secure an accurate admixture of the metals with it, because it will infallibly oxidate a portion of the copper, and, consequently, insure a somewhat finer alloy than the quantities introduced would make, if thoroughly amalgamated.

This, however, is a matter of little consequence in practical operations, as the loss is trifling, unless excess of borax is used.

There is a peculiar class of alloys, termed *solders*, which, melting at a lower temperature than the alloys with which they are used, serve to unite pieces of work to one another. It is necessary that they should flow smoothly and harden quickly, in order that they may be worked with facility. The common *gold solder*, for 18 carat gold, is composed of 66.6 parts of gold, 18 carats fine, 16.7 of silver, and the same quantity of copper. The following recipes for solder are copied from Dr. Harris's work on Dental Surgery:—

No. 1.

2 pennyweights 22 carat gold.
16 grains fine silver.
12 " rose copper.

No. 2.

1 pennyweight, 15 grains, 22 carat gold.
16 grains fine silver.
12 " rose copper.

No. 3.

6 pennyweights pure gold.
2 " rose copper.
1 " fine silver.

The latter is said to fuse with more difficulty, but to work better than the others. It is, in fact, 16 carat gold. Zinc has been added to these solders, for the purpose of making them melt more easily, but is objected to on account of the unpleasant brassy taste communicated by it to the mouth.

It will be seen, by what has been just said, that a thorough understanding of the subject of alloys is very necessary to all workers in metal. It would be too tedious, however, for the practical man to go through the labor of analysis and parting, in order to obtain pure materials wherewith to form his alloys. The form in which the precious metals are most commonly used is that of the coins of various nations. A table of these coins is, therefore, very necessary to all who work in the precious metals. The following is taken, with some alteration, from Eckfeldt's work on coins:—

Table of Coinage of Different Nations.

Nation.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
Argentine Republic.				
Doubloon, Province of Rio de la Plata,	1828–32	418	815	14 66
" " "	1813–32	415	868	15 51
The same variations of fineness and weight in coins of the same date are to be found in the silver coinage of this republic.				
Austria.				
Ducat of Maria Theresa,	1762	53.5	985	2 26 9
Sovereign of Maria Theresa,	1778	170	917	6 71 3
Ducat of Leopold II.,	1790	53.5	986	2 27 2
" of Francis I.,	1809–34	53.7	983	2 27 4
Quadruple of Francis I.,	1830	215.5	983	9 12 2
Sovereign of Francis I.,	1831	174.5	898	6 74 8
" of Ferdinand I.,	1838	174.5	901	6 77 1
Half-sovereign of Ferdinand I.,	1839	87	902	3 38
Ducat of Ferdinand I.,	1838	53.7	985	2 27 8
Quadruple of Ferdinand I.,	1840	215.5	985	9 14
Hungary ducat of Ferdinand I.,	1839	53.7	986	2 28 1
Baden.				
Ten guilder (five guilder same quality) of Louis, Grand Duke,	1819	105.5	900	4 08 6
Bavaria.				
Ducat of Maximilian Joseph and Charles Theodore,	1764–97	53	980	2 23 7
Ducat of Maximilian Joseph II.,	1800	53	984	2 24 6
" of Louis,	1832	53.5	987	2 27 4
Belgium.				
Forty francs,		199	895	7 67
Twenty francs in proportion, same fineness. Sovereigns same as Austrian coinage.				
Bolivia.				
Doubloon,	1827–36	416.5	870	15 58
Brazil.				
Moidore of Maria I. and John III.,	1779	125.5	914	4 94
Half-Joe of Peter II.,	1833–38	221.5	915	8 72 7
The other moidores and half-joes are of the same fineness with the moidore of 1779, varying slightly in weight.				
Britain.				
The gold coins of this kingdom are of the uniform fineness of 915.5, but below the legal standard about one-thousandth. The par value of the pound sterling is about $4 84. Sterling gold is worth 94.6 cents per pennyweight.				

TABLE OF COINAGE OF DIFFERENT NATIONS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
BRUNSWICK.				
X. Thaler of Charles,	1745	202	898	7 81 2
" of Charles William Ferdinand,	1805	204	896	7 87 2
" of Wm. Fred. and George, Regent,	1813–19	204.5	896	7 89 1
" of Charles,	1824–30	205	896	7 91
" of William,	1831–38	205	894	7 89 3
V. Thaler of Charles,	1748–64	102	903	3 96 6
CENTRAL AMERICA.				
Doubloons,	1824–33	417	833	14 96
CHILI.				
Doubloons,	1819–34	417	867	15 57
"	1835 and seq.	417	872	15 66
COLOMBIA.				
Doubloon of eight escudos, Colombia, Bogotan Mint,	1823–36	416.8	870	15 61 7
" " Popayan Mint,	1823–36	416.5	858	15 39
" of New Granada, Bogata,	1837	416.8	870	15 61 7
Half-doubloon of Ecuador, Quito,	1836	209	844	7 59 6
Quarter-doubloon of Colombia, Bogota,	1823–36	104	865	3 87 4
" of Ecuador, Quito,	1835	104	844	3 78
Eighth-doubloon of Colombia, Bogota,	1823–36	51	865	1 90
" " Popayan,		51	852	1 87 1
These last coins vary in fineness from 849 to 854, and in weight from 44½ to 61½. The sixteenth-doubloons are of the same quality.				
DENMARK.				
Specie ducat of Frederick V.,	1749	53.5	988	2 27 6
" of Christian VII.,	1795–1802	53.7	979	2 26 4
Current ducat of Christian VII.,	1783	48	876	1 81 1
Christian d'or of Christian VII.,	1775	103	905	4 01 4
Double Frederick d'or of Frederick VI.	1813–39	204.5	895	7 88 2
EGYPT.				
Sequin fundoukli of Achmet III.,	1115 (1703)	53	958	2 18 7
" of Mahmoud I.,	1143 (1730)	39	940	1 57 9
" "	"	39	848	1 42 4
" of Mustapha III.,	1171 (1757)	39	781	1 31 2
" of Abdul Hamed,	1187 (1773)	39	786	1 32
" "	"	39	645	1 08 3
" of Selim III.,	1203 (1789)	39	690	1 15 9
Half-sequin fundoukli of Mahmoud II.,	1233 (1818)	18	670	51 9
Bedidlik, 100 piastres, of Abdul Majeed,	1255 (1839)	132.2	874	4 97 6
Nusflix, 50 piastres, "	"	66.1	875	2 49 1
Kairie Hastreen, 10 piastres, "	"	27	874	1 01 7
The first date given above is the year of the Hegira; the second, the Christian era.				

TABLE OF COINAGE OF DIFFERENT NATIONS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
FRANCE.				
Louis d'or of Louis XV.,	1726–73	124	897	4 79
" of Louis XVI.,	1786–92	116.5	900	4 51 6
Double Louis d'or of Louis XV.,	1744	250	902	9 71 1
" of Louis XVI.,	1786–92	235	901	9 11 9
Napoleon, 20 francs, of Napoleon,	1803–14	99.2	899	3 84 1
The subsequent gold coinage of France is of the uniform fineness of 899, except the twenty franc pieces of Louis Philippe, coined in 1840–41, which are 900.				
GREECE.				
Twenty drachms of Otho,	1833	89	900	3 45
HANOVER.				
Ducat of George III.,	1776	53.5	993	2 28 8
Pistole or five thaler of George III.,	1803	102	896	3 93 6
" " "	1813–14	102	890	3 91
Ten thaler of George III.,	1813–14	204.5	890	7 83 8
" William IV. and Ernst. August.	1835 & seq.	205	895	7 90 2
HESSE.				
Ten thaler of Frederick II.,	1773–85	202	890	7 74 2
Five thaler of Frederick II.,	1771–84	101	893	3 88 4
" of William IX.,	1788–89	101.5	892	3 89 9
" of William I.,	1815–17	101.5	894	3 90 8
HINDOSTAN.				
Mohur of Bengal,	1770	190	982	8 03 5
" "	1787	191	989	8 13 4
" "	1793	191	993	8 16 8
" "	1818	204.7	917	8 08 4
" of Madras,	1818	180	917	7 10 9
" of Bombay,	1818	179	920	7 09 2
Half-mohur of Bengal,	1787	95	984	4 02 6
Star pagoda of Madras,		52.5	800	1 80 9
Pondicherry pagoda of Pondicherry,		52.5	708	1 60 1
Porto Novo pagoda, of Portuguese Company,		52.5	740	1 67 3
MECKLENBURG SCHWERIN.				
Ten thaler of Frederick Francis,	1831	204.5	896	7 89 1
MEXICO.				
Doubloon of Mexico, Augustin, Emperor,	1822	416.5	864	15 49 8
" " Mexican Republic,	1824–30	416.5	865	15 51 6
Other doubloons minted at Mexico weigh 417 grains, and are from 867 to 869 thousandths fine. The doubloon of Guanaxuato varies from 860 to 867 in fineness.				
Doubloon of Durango,		417	868	15 58 8
" "		417	865	15 53 4
" "	1833–36	417.5	872	15 67 9
" of Guadalaxara,		416	865	15 49 7

TABLE OF COINAGE OF DIFFERENT NATIONS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
MILAN.				
Zecchino, or Sequin, of Maria Theresa and Joseph II.,	1770–84	53.5	990	2 28 1
Doppia, or Pistole, of Joseph II.,	1783	97.5	908	3 81 3
Forty lire of Napoleon,	1805–14	199	899	7 70 6
Sovereign of Francis I.,	1831	174.5	898	6 74 8
" of Ferdinand I.,	1838	174.5	901	6 77 1
Half-sovereign,	1839	87	902	3 38
NAPLES AND SICILY.				
Six ducat, of Ferdinand IV.,	1783	135	893	5 19 2
Onzia of Sicily of Charles,	1751	68	859	2 51 6
Onzia of Ferdinand I.,	1818	58	995	2 48 5
Twenty lire of Joachim Napoleon,	1813	99	900	3 84 8
NETHERLANDS.				
Ducat,	1770–1810	53.5	980	2 25 8
" of William I.,	1833–39	53.7	981	2 26 9
Ten guilders of William I.,	1816–39	103.5	899	4 00 7
PERSIA.				
Toman of Fatha Ali Shah, Kajar, 1230–40 (1814–24)		71.2	991	3 04 2
" of Mohammed Shah, Shakinshah, 1255 (1839)		53.7	965	2 23 3
Half-toman of Mohammed Shah,	1252 (1837)	27	968	1 12 1
POLAND.				
Ducat of Stanislaus Augustus,	1791	53.5	984	2 26 6
PORTUGAL.				
Moidore of Peter II.,	1689	165	908	6 45 2
" "	1705	165	928	6 59 4
" of John V.,	1714–26	165	913	6 48 8
Half-joe,	1727–77	217	914	8 62
" of Maria I. and Peter III.,	1778–85	220	913	8 65
" of Maria I.,	1787–1804	221	914	8 69 9
" of John VI.,	1822–24	221	909	8 65 2
Joannese of John V.,	1730	439	912	17 24 2
Crown of Maria II.,	1838	148	912	5 81 3
PRUSSIA.				
Frederick d'or of Frederick II.,	1752–82	102	901	3 95 8
" of Frederick William II.,	1795–96	102	897	3 94
" of Frederick Wilhelm III.,	1799–1812	102	901	3 95 8
Double Frederick d'or of Fred. Wilhelm III.,	1800–11	205	898	7 92 3
" " "	1831	205	903	7 97 2
Ducat of Frederick William II.,	1787	53.5	979	2 25 6
ROME.				
Sequin of Pius VI.,	1775–83	52.5	996	2 25 2
Doppia of Pius VI.,	1777–86	84	906	3 27 8
" of Pius VII.,		84.5	901	3 27 9
Gold scudo of Republic,	1799	910	833	32 64 6
Ten scudi of Gregory XVI.,	1836	267.5	900	10 36 8

TABLE OF COINAGE OF DIFFERENT NATIONS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
RUSSIA.				
Imperial of Elizabeth,	1756	253	915	9 97
The gold coins of Russia, though irregular in weight, are of the same standard fineness during the reigns of Elizabeth and Catharine II.				
Ducat of Paul I.,	1798	66	969	2 75 4
Three roubles of Nicholas,	1838	60.5	917	2 38 9
Half-imperial of Nicholas,	1839	100.5	917	3 96 9
SARDINIA.				
Pistole of Victor Amadeus, &c.,		148	905	5 76 8
Carlino (island) of Victor Amadeus, &c.,	1773	247	890	9 46 7
Marengo of Republic,	1800	98	898	3 79
Eighty lire,		398	898	15 39 2
Genovine of Ligurian republic (Genoa)	1798	388	908	15 17 2
SAXONY.				
Double August d'or of Fred. August. III.,	1784–1817	204.5	896	7 89 1
" " "	1826	205	898	7 92 8
Double Anton d'or of Anthony,	1830–36	205	900	7 94 6
Ducat of Anthony,	1830	53.7	979	2 26 4
SPAIN.				
Cob doubloon of Philip V., American,	1733–44	416	895*	16 03 4
Doubloon of Ferdinand VI., American,	1751	416	908	16 26 5
" of Charles III., American,	1772–84	416	843†	16 00
" of Charles III., Spanish,	1786–88	416	890	15 58 7
" of Charles IV. and Ferdinand VII., American,	1789–1821	416.5	868	15 57
Pistole of Philip V., Spanish,	1745	103	909	4 63 2
" of Charles III., American,	1774–82	103	895	3 97
" of Ferdinand VII., American,	1813–24	104	872	3 90 6
Escudo of Charles III., Spanish,	1786–88	52	874	1 95 7
" of Charles IV.,	1789–1808	52	868	1 94 4
" of Ferdinand VII., American,	1809–20	52	851	1 90 6
Half-doubloon of Charles III., Spanish,	1780–82	206	896	7 95
" of Charles IV., American,	1789–1808	208	870	7 79 3
" of Ferdinand VII., Spanish,	1810–24	208	865	7 74 8
SWEDEN.				
Ducat of Gustavus III. and Gustavus IV.,	1777–1800	53	977	2 23
" of Charles John XIV.,	1838	54	975	2 26 7
SWITZERLAND.				
Pistole of Berne,	1796	116	901	4 50 1
" of Basle,	1795	118	891	4 52 8
" of Soleure,	1798	116	898	4 48 6
" of Helvetian Republic,	1800	116	897	4 48 1
Ducat of Berne,	1794	52.5	974	2 20 2
" of Basle,		53	943	2 15 2

* Varies from 893 to 898.

† Varies from 883 to 893, the oldest pieces being the best.

TABLE OF COINAGE OF DIFFERENT NATIONS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
TUNIS.				
Half-sequin of Abdul Hamed,	1773	19	885	72 4
TURKEY.				
Sequin fondouk of Selim III.,	1789	52.5	800	1 80 9
" zermahboub of Selim III.,	1789	36	800	1 24
Ohikilik of Mahmoud II.,	1822–24	25	833	89 7
Twenty piastres of Mahmoud II.,	1827	27.5	875	1 03 7
Yirmilik, 20 piastres, of Abdul Medjid,	1840	24.5	832	87 7
TUSCANY.				
Ruspone of Francis III. to Leopold III.,	1738–1800	160	997	6 87
" of Louis I. and Charles I.,	1801–07	161	998	6 91 9
" of Leopold II.,	1824–34	161	999	6 92 5
Sequin of Leopold,	1765–79	53	997	2 27 6
" of Leopold II.,	1824–34	53.5	999	2 30 1
UNITED STATES.				
Eagle,	1792–1834	270	916.7	10 67 4
"	1834–1837	258	899.2	9 99 7
"	1837 and seq.	258	900	10
WURTEMBERG.				
Ducat of Charles,	1790–1818	53	980	2 23 7

Articles of jewellery were formerly rarely to be found in the melting pots of the goldsmith, but fashion now changes their form almost as rapidly as it does that of less costly toys. They are extremely irregular in their composition. As a general thing, however, the percentage of fine gold contained in them is small. It may be said to average in American jewellery from 12 to 14 carats. Often, in bulky articles, the core or basis of the jewel is made of some cheap alloy, which is covered so thickly with the gold that it can hardly be said to be plated. The British standard for jewellery is 22 to 18 carats; the French, $22\frac{1}{16}$, $22\frac{1}{8}$, and 18; the Austrian, $18\frac{5}{12}$ and $13\frac{1}{12}$; the Mexican, 20. These qualities are usually stamped.

Jewellery is subject to a very great loss in melting, which varies with the kind subjected to the action of the fire. Part of this is owing to the dirt which accumulates in the numerous cavities, part to the quantity of solder used in the construction of the pieces. This sort of bullion is always refined with nitre.

SALTS OF GOLD.

The salts of gold are few and imperfectly known. The sulpho-salts are usually combinations of some sulphacid with the sesquisulphuret of this metal. Thus the sulpharseniate of gold is composed according to the formula $2Au_2S_3$, $3As_2S_3$.

Oxide of gold also enters into triple combinations with some of the oxacids and another base. Thus, hyposulphite of potassa or soda attacks the oxide of gold and forms with it durable salts, dithionites of the alkaline base and of protoxide of gold. If terchloride of gold be added, in successive portions, to hyposulphite of soda until the yellow color disappears, and the solution then be evaporated to the point of crystallization, the greater part of the hyposulphite and sulphate of soda separates. The liquid again crystallized yields, among others, colorless needles, which, by solution in alcohol of 0.9 and spontaneous evaporation, furnish the same crystals. They are probably dithionite of soda and gold.

The haloid salts, however, are the most numerous and best understood. They are yellow or orange color; let fall the purple of Cassius with the salt of tin when very dilute, and metallic gold as a brown impalpable powder with protosulphate of iron, and other deoxidating reagents.

Chlorides.—1. The *protochloride of gold*, AuCl (234.62), is formed by evaporating the terchloride and heating it in a porcelain basin to about 450°, with constant stirring until chlorine is no longer given off. At a higher heat, but below redness, it is completely decomposed, all the chlorine being dispelled, and metallic gold left. Hot water completely decomposes it, resolving it into terchloride and metallic gold, and potassa converts it into protoxide of gold, chloride of potassium remaining in solution.

2. *Terchloride of Gold*, $AuCl_3$. 305.46.—This is the form in which gold is usually obtained in solution, and the salt which is applied to the greatest number of practical purposes in the arts. The method of obtaining it has already been described. When the entire solution of the gold is not an object, the ex-

pulsion of nitric acid is most conveniently effected by using an excess of metal. When crystals are to be made, the solution thus obtained is to be evaporated on a water-bath, at a very gentle heat; when the concentration is sufficient, the solution is removed, and crystallizes immediately on cooling. As the salt is highly deliquescent, it must be bottled at once in well-closed and warmed phials. The crystals must be dried rapidly, but without any increase of heat, as it is fusible at a very low temperature, and decomposed at 300°. The crystals are acicular, and of a brilliant ruby-red color.

The solution is yellow when dilute, deep orange-red when concentrated. It is reduced in part in a closed glass vessel, on one side of which metallic gold is deposited. It is reduced by phosphorus, hydrogen, phosphuretted hydrogen, sulphurous acid, and the sulphites, nitric oxide, peroxide of nitrogen, and nitrite of potassa in the cold, and by sulphur and selenium with the aid of heat. It is reduced by most of the metals, by arseniuretted and antimoniuretted hydrogen, terchloride of antimony and white arsenic, and protosalts of iron. Protochloride of tin precipitates brown gold-tin from a strong, and purple of Cassius form a weak solution. Protonitrate of mercury gives a dark blue precipitate. It is also reduced by most organic bodies, whether in solution or not, especially by the addition of potassa. Oxalic acid and oxalate of ammonia precipitate gold in very thin leaves. Potassa, soda, strontia, lime, magnesia, and oxide of zinc throw down the greater part of the gold as an impure oxide or a basic salt, the precipitate by the last two being easily purified by nitric acid. Sulphuretted hydrogen throws down sulphuret of gold soluble in alkaline sulphurets. Ammonia precipitates a bright yellow substance, which is a basic salt mixed with fulminating gold.

Chloraurides.—The terchloride of gold combines directly with nearly all the metallic protochlorides, forming compounds which contain 3 equivalents of chlorine in the chloracid to 1 in the chlorobase. They are almost all orange-colored in the crystallized state, becoming paler yellow by efflorescence, but deep red when anhydrous. The *chlorauride of potassium* will serve as the type of these compound salts. The anhydrous salt is composed

according to the formula KCl, $AuCl_3$, and contains 52.4 per cent. of gold. The crystals are expressed by KCl, $AuCl_3 + 5HO$, and contain 46.84 per cent. of metallic gold. These crystals are rhombic prisms or six-sided tables, efflorescent, losing water at 212°, without farther decomposition, soluble both in water and alcohol. At a higher heat than the boiling point of water, they are converted into double protochlorides.

Bromides.—The *terbromide of gold*, formed by dissolving the metal in nitrohydrobromic acid, is obtained by evaporation as a red mass, which combines with metallic bromides to form bromaurides, in the same manner as the terchloride forms chloraurides. These salts are hydrated and purple or brownish-red in tint.

Iodides.—*Protiodide of gold*, AuI. 325.5.—This salt is formed in several ways. It may be obtained by the action of hydriodic acid upon oxide of gold, or the finely divided metal, in which latter case it must be aided by nitric acid; or, lastly, by double decomposition, the terchloride being treated with iodide of potassium. The latter agent must be added gradually to a solution of the terchloride till it ceases to produce a precipitate. A yellowish crystalline powder falls, which is to be washed first with alcohol and then with water. This substance is decomposed by acids only when heated, readily by alkalies, by hydriodic acid, iodide of potassium and of iron.

Teriodide of Gold, AuI_3. 578.1.—This salt is prepared by adding gradually terchloride of gold to a dilute solution of iodide of potassium, till it becomes dark-green. The liquid is then agitated till the precipitate is redissolved, and more terchloride added, which precipitates the teriodide. It is dark-green, easily decomposed, soluble in hydriodic acid, forming a dark-brown crystallizable solution, and unites with basic iodides to form iodaurides, analogous to the chloraurides and bromaurides already adverted to.

CHAPTER III.

SILVER.

This is also a long-known metal. The most ancient of books, Job, speaks of it, and we are told that Abraham was rich in silver and gold. It is not so universally found native as gold, and requires more art to extract it from its ores; yet its greater abundance gives it a lower relative, and its inferior resistance to oxidating and corroding agents a less positive value than the last described metal. The mediæval writers called it a *perfect* metal, because it could be revived from its oxide by the simple application of heat, and because it could resist the fiery *experimentum crucis* which, to their imperfect apprehensions, seemed to destroy the baser metals. Its correlative planet, in that singular astro-chemical system, was the moon, as that of gold was the sun. This old nomenclature is still retained, to a certain extent, in the common language of the apothecary. Fused nitrate of silver is still called *lunar caustic*, and the arborescent form of the precipitated metal bears its ancient name, *Arbor Dianæ*.

Silver is found native in most of the mines in which this metal is worked. Its crystals are octohedral, or cubic, or have forms derived from these. Sometimes it is found dendritic, the arborescence being composed of minute crystals connected together. Again, it occurs in filaments, perforating the vein stone in all directions, and in sheets coating the surface of the rocks or filling up its seams. At the Lake Superior copper mines, it is found in the native copper in small cavities, called by the workmen pockets or purses. Large masses of it, some of them weighing many hundred pounds, have also been met with. The metals most commonly alloying the native silver are gold, arsenic, copper, and iron. The usual form in which this metal is obtained is a sulphuret, combined with lead, copper, antimony, or iron. It is more frequently mixed with lead than with

any other metal. But little galena can be found which does not contain a trace at least of silver. Chloride of silver, or horn silver, is occasionally met with. The carbonate is rare as a native product.

METALLURGIC TREATMENT OF SILVER ORES.

The treatment of the ores of silver varies with the nature of the ore itself. There are two prominent modes of working them—smelting and amalgamation. The former method is used for the richer, the latter for the poorer ores. Argentiferous galena is first smelted to obtain silver-lead, and then either crystallized or cupelled to separate the more valuable metal. The process of amalgamation varies in different places. The method of Mexico and that of Saxony are the two prominent ones, and a brief sketch of them will suffice to give a general view of the process.

AMALGAMATION.

Mexican Method.—The ore is prepared for amalgamation by stamping it finely in a mill, and then reducing this stamped ore to a thin mud, by crushing it with heavy rollers or crushers under water. The more minute and thorough this division of the ore, the more completely will the quicksilver unite with the metal. This metalliferous mud is transferred to the *patio*, or amalgamation floor, and there mixed with *saltierra*, a coarse impure salt, and thoroughly incorporated by shovelling the heaps over and over, and trampling them with horses' hoofs. A *magistral*, obtained by roasting copper pyrites, is then stirred in and very completely mixed, as before, by trampling. Lime is sometimes added. The materials now being all prepared, the mercury is introduced by sifting it through a coarse canvas bag. The mass is now trodden again by horses, and turned over with shovels until the amalgamation of the first quantity of mercury is found to be complete, a state of things determined by a simple washing assay. More mercury is then added, and when it has taken up all the silver it can, another portion is added, and so on till the silver is exhausted. The amalgamated ore is now

transferred to vats of water, in which horizontal beams, set with long wooden teeth, are made to turn with great rapidity. The water is thus briskly agitated, and this motion insures, after a time, the perfect separation of the lighter earthy matters from the heavy metallic amalgam. The latter settles to the bottom, and is afterwards collected and subjected to heat in a distilling apparatus, which drives off the mercury and leaves the porous silver behind. This is cast into bars of about 1,080 ounces each. The loss of silver is about five ounces to each bar, that of mercury, from $2\frac{1}{2}$ upon the finer ores to 9 upon the coarse.

The chemical changes effected in the ore by this process may be thus explained. The *magistral*, or combined sulphate of iron and copper, being mixed with the salt, a double decomposition ensues, the chlorides of iron and copper being formed on the one hand and sulphate of soda on the other. The deutochloride of copper reacts upon the silver, converting it into chloride of silver, and becoming itself protochloride of copper. The mercury, in presence of the saline menstruum, reduces the chloride of silver, and the remaining quicksilver amalgamates with the silver. The chloride of mercury thus formed is partially decomposed by the sulphate of silver resulting from the direct reaction of the sulphates on the silver. Quicklime counteracts the injurious effect of too much *magistral*, by decomposing the resulting sulphate.

Saxon Method.—The ores for amalgamation by this process are carefully selected, and so mixed that their average yield shall be from $3\frac{3}{4}$ to 4 ounces in the 100 pounds.* All those which contain more than 7 per cent. of lead, or 1 per cent. of copper, are rejected, because the lead would render the amalgam very impure and the copper would be wasted. It is necessary that the ores contain a certain proportion of sulphur, that they may decompose enough salts, during the process of roasting, to disengage chlorine sufficient to convert all the silver present into a chloride. The ores, having been selected and mixed in due proportion, are now incorporated with 10 per cent. of their weight of common salt. The salted ore is then roasted, with frequent stirring, at first at a low temperature, just heat enough being applied to keep the mass at dull redness, and then, when the conversion of

the sulphur into sulphuric acid is complete, at a higher temperature, sufficient to decompose the sulphates, converting them into chlorides with the simultaneous formation of sulphate of soda. The ore having been brought into this condition, is now ground and bolted to an impalpable powder.

The finely comminuted ore is introduced into casks containing 3 cwt. of water to every 10 cwt. of ore. Into this mixture are thrown scraps of iron, which are renewed as fast as they are dissolved. These decompose the metallic chlorides, throwing down metallic copper and silver in a finely divided state. The casks are now set to revolve horizontally, till the ore and water are reduced to a uniform pap, which must not be too thin, or the mercury will sink to the bottom; nor too thick, or it will float on the surface. The mercury is now introduced, one-half the weight of the ore, and the barrels are made to revolve 22 times in the minute. This combines the metals with the quicksilver in a complex amalgam. During this change, the temperature rises so that, even in winter, it sometimes stands so high as 104° Fahrenheit.

The amalgamation being completed, the casks are filled with water and revolved slowly till the amalgam collects at the bottom. This is drawn off, and is found to have exhausted the silver very completely, the metal remaining in the ore amounting to not more than .15 to .18 of an ounce per cwt. The quantity of mercury used amounts to .95 of an ounce for every pound of silver obtained. The amalgam is now poured into wet canvas bags and pressed, to get rid of uncombined quicksilver, and then placed in a peculiar distilling apparatus, when the mercury is volatilized and a porous mass of metal remains behind, which contains the silver mixed with copper, lead, bismuth, nickel, antimony, cobalt, zinc, arsenic, and iron. This is refined by cupellation. The silver remaining in the casks is submitted to a fresh amalgamation.

SMELTING.

This process presents nothing peculiar. It is only the comparatively rich ores that can be worked in this way, and very

large losses have been sustained by attempting to smelt ores which were not adapted to this method of working. The ores best suited to it are those which are composed of the mixed sulphurets of lead, or copper and silver. These are smelted with the addition of iron, by means of which a lead is obtained rich in silver, and a slag containing lead, copper, and silver. This lead-stone, as it is called, is roasted and smelted again. A similar division into a silver-lead and a lead-stone takes place, and the roasting and smelting are continued as long as the quantity of metal obtained pays for the labor and materials used to separate it.

METALLURGIC TREATMENT OF THE ALLOYS OF SILVER.

The management of alloys of silver differs with the nature of the alloy and the amount to be operated upon. In the small way, alloys may be treated either by the dry or the humid method, but on the large scale, the dry process alone can be employed. The first-named processes will be first described, and then the modifications of them which are necessary in order to work successfully on the great scale.

When the mixed metals are contaminated with much earthy matter, as the sweepings of a silversmith's shop, the fragments of old crucibles which have been used for melting silver, &c., it is necessary first to get rid of these earthy matters by fusion with carbonate of soda or borax. Black flux, which is an intimate mixture of charcoal and carbonate of potassa, has been used for the same purpose. Nitre is advantageously combined with these fluxes, as it oxidates the baser metals at the same time that it assists to flux the earths. Litharge is also used for this purpose, as well as for the oxidation of sulphurets and the more oxidizable metals.

SCORIFICATION.

This process is commonly used in the assay of silver ores, especially the sulphurets, but is also applicable to the reduction of alloys, more particularly that of tin and silver, two metals very difficult to separate in the dry way.

This operation is performed in deep saucers of refractory earths called scorifiers, which are heated in the muffle of a cupelling furnace. The ore or alloy is reduced to a state of minute division, mixed with granulated lead and borax, and introduced into the scorifiers. Lead may be used alone, but the addition of borax facilitates the operation and protects the scorifiers. A gradual heat having been first applied, the door is closed, and the fire pushed to fuse the materials, and then, the door being opened again, a current of air is admitted, and the roasting or oxidation begins. Fumes, of colors varying with the character of the burning substances, are now given off, a movement is observed upon the surface of the bath, the scoriæ are thrown to the sides, forming a ring, in the centre of which is the fused metal, constantly diminishing in size as the oxidation advances. The borax dissolves the oxides as fast as they are formed, and keeps the slag perfectly fluid during the entire operation. There is obtained, as the result of this process, an alloy of lead and silver, which is to be cupelled.

The proportion of lead and borax varies. For alloys containing zinc or tin, much of the latter reagent must be used. For the tin alloy, 16 parts of oxide of lead and 3 of borax are the best proportions.

CUPELLATION.

This is a very ancient process for the separation of the precious metals from their alloys. It depends for its success upon the property of certain oxides to soak or filter through the pores of the cupel, while the fused metals remain upon its surface. Much depends on the skill of the workman, much on the structure of the cupel. The latter should be sufficiently loose in texture to enable the fused oxides to pass through with ease, and yet solid enough to bear the necessary handling. It should also be made of a substance which is infusible in the oxides of lead or bismuth, as these are the only substances used in this operation, they alone possessing the property of passing through the cupel and of carrying other oxides with them.

This operation is conducted in a muffle. The furnace is

heated, the cupels introduced and kept empty till the inside of the muffle is reddish-white. Care having been taken to remove all foreign matters which may have fallen into the cupels, the substances to be experimented on are now put in. If they are alloys which contain the necessary amount of lead to carry off all the oxides through the pores of the cupel, they are directly introduced; if not, they are first wrapped in a sheet of lead of the necessary weight, or fused with litharge, or laid carefully on a bath of metallic lead previously fused in the cupel. When they are in small grains, it is well to wrap them in a very thin sheet of lead and drop them into the metallic bath.

The muffle is now closed, either by the door or by pieces of charcoal, till the alloys have been brought to the same temperature with the muffle. When this point has been attained, air is admitted. The metal, which has been very smooth with a convex surface, becomes very lustrous as soon as the air touches it. Bright iridescent patches make their appearance. Glancing lights flash over the surface, and pass off to the sides in rainbow-colored rings. This is due to the formation of the oxide of lead, which, being absorbed by the cupel as fast as it is formed, is perpetually covering and uncovering the metallic bath, and giving rise to the motion from the centre to the circumference. At the same time a lead-vapor rises and fills the muffle, and there is formed round the metal a ring, which continually increases till it reaches the edge. The metallic bath regularly diminishes during the progress of this operation, the shining points on its surface become larger and move more rapidly; at last the button is agitated by a rapid movement, which causes it to turn round on its axis. Then it remains quiet, and, though dull at first, soon assumes the appearance of pure silver. This last stage has been termed the *brightening*, *fulguration*, or *coruscation*.

The cupel must be gradually cooled, or the assay will *vegetate;* that is, it will be covered with small protuberances over its surface, and it may even spirt out and cause a loss of silver. This has been attributed to the sudden contraction of the surface of the metal, produced by rapid cooling, while the centre of the mass is still fluid. It may, in part, be due to this cause, but

more probably to the escape of absorbed oxygen, as will be hereafter explained.

The proper management of the temperature is a matter of great importance to the success and economy of this method of reducing silver. If the heat be too high, some silver will be volatilized; if too low, the same thing will take place on account of the length of time necessary to complete the reduction. The suitable degree of heat is ascertained by the bright redness of the cupel, and the clear, luminous appearance of the melted metal. If the cupels are white, the metal scarcely visible, the fumes indistinct and rising rapidly to the arch of the muffle, the furnace is too hot. If, on the other hand, the smoke is thick and heavy, and falls in the muffle, and if the litharge forms lumps and scales about the metal, it is not hot enough. It is best to give a strong heat at first, then to cool down a little, and, towards the end of the process, to increase the temperature again. The operation is usually more successful at too high than at too low a heat.

The force of the current of air which passes through the muffle is also a very important circumstance. Too strong a current cools the cupel, and oxidates the lead too rapidly; too feeble a one renders the operation so slow that much silver is volatilized. If the operation has been successful, the button will be well rounded, white, crystalline below, and easily detached from the cupel.

Cupellation, however carefully conducted, never separates from the alloy the entire amount of silver. There is always some of the precious metal lost by volatilization, a notable proportion of it being found in the dust or soot deposited by the lead vapors already described as filling the muffle during the operation. Silver is also lost by oxidation, in which case it penetrates the cupel, and there is a farther loss arising from the tendency of the silver-lead to pass into the cupel. The total amount of loss for alloys rich in silver has been estimated at .0003, or .03 per cent., and for the poorer alloys at .002, or 2 per cent.

In selecting a cupel, there is no difficulty, if the necessary

amount of lead be known, for these little instruments absorb their own weight of litharge.

The metals contained in the alloy are indicated by the appearance of the cupels after the operation has been concluded. Pure lead colors the cupel straw-yellow verging on lemon-yellow; bismuth, straw color passing into orange; copper, a gray, dirty red or brown; iron produces black scoriæ, found at the circumference of the cupel; tin forms a gray slag. Zinc leaves a yellowish ring on the cupel, becoming white as it cools. Antimony and sulphate of lead produce yellow scoriæ which crack the cupel.

The modifications of this process for reducing silver on the large scale are confined entirely to matters of detail. The cupel is made upon the base of a large furnace hearth, which usually contains several layers; first, the masonry of the foundation, then, a bed of hard rammed scoriæ, and, lastly, bricks set on end, forming the permanent area of the furnace. Leached wood ashes from the soap factories constitute the material for these great cupels. They are sometimes mixed with lime, clay, marl, or bone-ash. They are well beaten in over the upper layer of the hearth. When the cupel is formed, it is a basin-shaped cavity, containing, in some works, a smaller cavity in the centre for the reception of the silver, and a gutter at the side to run off the litharge. In the Hartz Mountains, the furnaces have a movable iron dome which may be let down upon them during the operation, and one or more pair of bellows fixed in the side walls. The silver-lead is laid upon the hearth, and as soon as the ebullition of the melted metal has ceased, the bellows begin to play over the surface at the rate of four or five blasts to the minute. This oxidates the lead, and the heat being now urged, a grayish froth, composed of oxidized metals and impurities, makes its appearance. This is raked off, and then the clear litharge begins to form. This is also drawn off, the gutter being deepened as the level of the liquid falls. Towards the close of the process, the litharge becomes rich in silver, and is, therefore, laid aside separately from that which was first formed. The colored particles of oxide of lead now move with great rapidity over the surface; the alloy is less fusible, and the silver-cake is

soon perfectly formed. As soon as *fulguration*, or the total disappearance of the oxide of lead, takes place, the fire is checked, the bellows stopped, and a stream of hot water thrown upon the silver-cake. This is refined by a new cupellation in a more carefully made cupel.

The litharge of the cupel is now smelted to obtain metallic lead. The total loss of lead is estimated at 4 per cent. In the Frankensham works, much of this loss is obviated by conducting the smoke through long flues in which the lead fumes are condensed into a metallic soot.

In connection with this subject, it is proper to state an attribute of silver, discovered by MM. Lucas and Gay Lussac. They have proved that metallic silver, when fused in the air, absorbs oxygen and gives it out again in the act of solidification. The quantity thus absorbed may amount to twenty-two times the volume of the silver.

The phenomena presented by a large mass of the metal undergoing this process, are very peculiar. The consolidation commences at the edges and advances towards the centre. The liquid silver, at the moment of passing to the solid state, is agitated, and then suddenly becomes quiet. After remaining motionless awhile, the surface breaks up into several lines of fissures, and liquid silver flows out again, renewing the original agitation. Presently the gas is given off with great violence, and numerous little protuberances stud the whole face of the mass. Some of these are true volcanic cones. They have a crater, and the liquid silver, boiling violently, pours out through them over the superficial incrustation. The cones gradually increase in height, by the accumulation of metal. The surface of the metallic crust on which they rest is now violently agitated, being heaved up and falling again in great undulations. At last some of the craters close, and more work is consequently thrown upon those which still continue to give exit to the gas. The funnels are now lengthened, and proportionally contracted. The globules of silver are now projected with greater force, being carried beyond the furnace. A series of explosions accompanies the expulsion of these ejected masses. The last remaining crater is that which exhibits this volcanic action in

its greatest energy. It is a remarkable coincidence with the known geological history of volcanoes, that these cones are not all equally active, some having spent their force and become closed, while new ones are rising. During this action, portions of silver are shot forth, which assume, on cooling, cylindrical or fantastic shapes.

LIQUATION.

This process, which is more commonly known as *sweating*, is based on the various fusibility of metals and their different affinities for one another. It is sometimes applied to the separation of the easily fused metals from their stony matrices, and sometimes to the extrication of certain metals from their alloys.

A furnace of a peculiar construction is used for this purpose. It consists essentially of two walls sloping towards each other, upon which are laid the liquation or refining plates. These are plates of iron, which, like the walls, incline towards each other, leaving an opening between them, through which the melted metal may drip.

This process is applied especially to the reduction of the argentiferous copper of Germany. The copper having been first smelted, is mixed with lead, in the proportion of 3 or 4 parts of the former metal to 10 or 11 of the latter, and the resulting alloy is broken into small masses. These are laid on the liquation hearth, and the proper heat applied by coals which cover them. Most of the lead runs down into the chamber below, carrying the silver with it, and leaving on the hearth the copper alloyed with from 10 to 30 per cent. of lead.

CRYSTALLIZATION.

This process of refining has been introduced by Mr. Pattinson, of Newcastle, England. It is exceedingly economical, the loss of lead amounting to no more than 2 per cent., so that it is profitably applied to alloys too poor in silver to be submitted to cupellation. The process is based upon the behavior of an alloy of silver and lead remaining long in fusion.

When an alloy of this kind is allowed to cool very slowly,

with constant stirring, crystals are formed which are poorer in silver than the original alloy. The liquid metal, therefore, retains excess of silver. These crystals may be lifted out and drained as fast as they are formed, so that the fused metal contains a continually increasing proportion of silver. By this process, the poor lead is brought to the ordinary standard of alloys designed for cupellation, while the better lead is made ten times richer. The necessary loss is, therefore, reduced to one-tenth of what it is under the old process, so that it becomes $\frac{7}{10}$ of one per cent. instead of 7 per cent.

The practical details of the operation are very simple. In the improved method, a series of seven pots is used, each of which is heated by a separate fire. The crystals which are formed in the first of these, and which still contain some silver, though much less than that which remains in fusion, are lifted in a drainer and emptied into the second pot. Here a second crystallization takes place, which results in a farther impoverishment of the crystals. These are transferred to the third pot of the series, and the enriched mass returned to the first. This constant shifting of the products of each crystallization is continued till pure marketable lead is taken out of one end of the apparatus and a rich alloy of lead and silver from the other.

HUMID PROCESS.

In the humid way, silver is separated from its combinations with other metals in several ways; the two most important of which are the separation of the metal by copper, and of the chloride by common salt or hydrochloric acid.

When silver is alloyed with copper alone, neither of these methods presents any difficulty. In any case, the alloy is dissolved in dilute nitric acid with the aid of heat. If the precipitation as metallic silver is determined upon, strips of pure copper are introduced into the solution, which is then gently warmed till all the silver is deposited, which may be known by the solution no longer affording a precipitate with hydrochloric acid. The silver is thrown down in a pasty form. The remainder of the copper slips is then removed, and the precipitate thoroughly

washed in warm water. It is then digested for some time with ammonia, in order to remove any adhering copper, washed again with warm water, dried, and fused with a little borax or saltpetre. The objections to this process are that other metals besides silver are precipitated by metallic copper.

When the separation of silver as a chloride is determined upon, the nitric acid solution of the alloy is treated with dilute hydrochloric acid, or with chloride of sodium (common salt) in solution, so long as a precipitate is thrown down. A white curdy precipitate, which becomes dark on exposure to light, makes its appearance, and slowly subsides to the bottom of the vessel. Agitation facilitates both the formation and the subsidence of the precipitate. The chloride of silver is now repeatedly washed with clear, pure water, till all trace of acid has disappeared. The water poured off after each washing must be transferred to a deep glass jar, and, if not perfectly clear, must be allowed to stand for several hours in a warm place. Should any precipitate form, it is added to that previously obtained.

The reduction of the chloride to metallic silver is effected in two ways, by fusion with carbonate of potash, or by dechlorinizing it by a stream of hydrogen gas. In attempting the reduction by the first-named method, it is necessary first to dry the chloride thoroughly, and then to rub it to powder in a stone mortar. The carbonate of potash, in the proportion of 2 to 1 of silver, is then fused in a black-lead or Hessian crucible, taking care not to fill it more than half full, for there will be much loss by ebullition should this precaution be neglected. The carbonate of potash having been brought to a state of fusion, the chloride of silver is projected, in small portions at a time, into the melted salt. Violent effervescence takes place, in consequence of the rapidity with which the carbonate of potash is decomposed, and carbonic acid and oxygen gases driven off. The result of the double decomposition is, that the carbonate having lost the last two named gases, potassium remains, which combines with the chlorine of the silver salt, and metallic silver subsides. At first, the heat should not be higher than a full red, but, so soon as the violence of the action has ceased, the temperature is increased to a reddish white, in order to insure

the perfect fusion of the silver and its complete separation from the slag. The metal may then be most conveniently separated from the slag by pouring it into water from a height, when the chloride of potassium is at once dissolved and the granulated silver subsides. Some loss, however, is occasionally experienced in this way, especially if the metal be very hot and in large quantities, when it sometimes explodes with great violence, projecting globules of silver to a considerable distance beyond the vessel.

Wittstein affirms that the most economical method of reducing the chloride of silver is to heat it with wet charcoal. He mixes 2 parts of the chloride with 1 part of moist charcoal, packs the mixture in a black-lead crucible, loosely covered, and calcines it till half an hour has elapsed after the cessation of the evolution of hydrochloric acid vapor. When cold, he extracts the silver from the mass by means of nitric acid of 1.20, 3 parts of the acid being required for two of the chloride. By giving the crucible a very high heat, the reduced silver will be fused into globules, which can be separated mechanically from the remaining charcoal. The reducing power of the charcoal depends upon the hydrogen it contains.

The reduction by hydrogen is preferable to the last described method, as it affords a perfectly pure silver without any perceptible loss. The chloride having been thoroughly washed, as already described, pieces of pure iron or zinc are introduced into it and sufficient sulphuric acid to disengage hydrogen. This gas streams up through the chloride, converting its chlorine into hydrochloric acid, which attacks the iron or zinc. During the formation of the chloride of the reducing metal, hydrogen is again set at liberty, and reduces another portion of silver, by separating the chlorine from it to form hydrochloric acid. This process goes on continually, till the entire precipitate is decomposed. The silver thus reduced is in a state of exceedingly minute subdivision, without the slightest metallic appearance, but resembling finely divided ashes more than anything else. The metallic lustre of silver can, however, be developed by pressing this ash-colored powder with any smooth, hard substance, such as glass or polished iron. The reduction is accomplished in a

day or two, and if the precipitate is in a state of sufficiently minute division, and enough sulphuric acid and reducing metal have been introduced, the reduction will be complete. It can easily be determined whether any chloride remains undecomposed by digesting the precipitate in water of ammonia, which dissolves the chloride and lets it fall again on saturation with an acid. The reduced silver must be washed first with acidulated water to remove any small adhering particles of iron or zinc, and then with pure water. After the washing, the silver is thoroughly dried, and fused with borax. It is best to mix the powdered glass of borax with the silver and project it in small quantities into the heated crucible. The same precautions should be observed in reference to the heat as have already been described under the head of Reduction by means of Carbonate of Potash.

This process is performed at the United States Mint, on about a thousand pounds of silver a day. Zinc is there preferred to iron, which is used by some silver-workers, on account of the greater facility of granulation, the greater rapidity of reduction, and the greater ease with which the residual zinc can be separated from the precipitated silver. Saltpetre and borax are used in fusing the silver. Without any special pains, by this process silver is obtained of a fineness of 995 to 997½ thousandths, and may be easily refined in the pot to 999 thousandths.

Kessler obtains absolutely pure silver by dissolving the alloy with copper or lead in nitric acid, diluted with 20 times its bulk of water, and adding a solution of protacetate of iron till a precipitate ceases to fall. This is washed till the mixings no longer give a precipitate with ferrocyanide of potassium. The silver is so entirely thrown down that common salt will not make the filtered solution turbid. The protacetate of iron precipitates platinum also.

Lovel uses sugar to reduce the chloride. He boils the salt in a solution of sugar in water of potassa. Gray metallic silver falls, and carbonic acid is evolved.

Rose has objected to the process with chloride of sodium, that the precipitation of the silver is not complete, this salt, as well as the chlorides of potassium and ammonium, retaining some

of the metal in solution. This objection, however, has weight only with the analytical chemist, as the loss of silver is so small as to be scarcely perceptible to the operator who is preparing it for mechanical purposes, and much too minute to pay the difference in cost between salt and muriatic acid.

It has been farther objected that mercury, when present in an alloy of silver, is precipitated by the chlorides along with the latter metal. Its presence can be recognized by the altered behavior of the precipitated chloride. When there are from four to five thousandths of mercury present, the chloride does not blacken at all, but remains of a dead white. When three thousandths are present, there is no marked discoloration in the diffused light of a room. With two thousandths the darkening is slight, and with one thousandth it is more marked, but still much less intense than when pure silver alone has been subjected to the action of chlorine. When these phenomena are present, it is best to purify the alloy in the dry way.

One of the most troublesome metals to the chemist, who is attempting the separation of silver from its alloy by this humid process, is lead. Very minute portions of this metal are precipitated from strong solutions by hydrochloric acid or the chlorides, and when large quantities of it are present, its chloride is precipitated from quite dilute solutions. When there is but little lead in the alloy, this difficulty is obviated by making the solution very dilute, and precipitating while warm. Should much be present, it will generally fall with the silver, and then may be distinguished by its obscure crystalline character, and its rapid heavy subsidence. It may be removed by repeatedly washing the mingled precipitate with boiling water, in which chloride of lead is soluble. In the small way, the two chlorides may be separated by means of ammonia, in which the silver-salt alone is soluble. A still simpler method is to precipitate the solution of silver-lead with a solution of chloride of lead. It is more convenient, however, to treat this alloy by cupellation.

Of the parting of silver from gold it is not necessary here to speak, that process having been already described in the chapter on Gold. It is proper, however, to state, that all goldsmiths' silver and most silver coin contain gold, which makes its ap-

pearance in dark flocculi, when the silver is dissolved in nitric acid. The separation of silver from platinum will be treated of under the head of the latter metal. Its separation from all other metals is effected with greater or less facility by the processes already described.

SILVER, NON-SALINE COMPOUNDS, AND ALLOYS.

Silver.—Silver varies in appearance according to the manner in which it has been obtained. The precipitated powder is, as already said, gray, devoid of lustre but assuming the brilliant appearance of metallic silver when forcibly compressed. When fused and planished, it is the most brilliant of the metals, and its clear white color is too well known to need any description. It is harder than gold, but soft enough to be cut with a knife, and exceedingly malleable and ductile. It may be reduced to leaves $\frac{1}{100000}$ of an inch in thickness, and drawn out in a wire much more slender than the finest human hair, so that a grain of it will be 400 feet in length.

It does not oxidate when exposed to air and moisture, but in cities it gradually becomes covered with a brownish-black tarnish, owing to the formation of a sulphuret of silver, in consequence of the action upon the metal of the sulphuretted hydrogen contained in the atmosphere of populous places. In salt air it also tarnishes, in consequence of the formation of a chloride. Its absorption of oxygen, when fused in the open air, has already been described. According to Brande, 5 per cent. of copper prevents this action. When heated to redness, without melting, in contact with glass or porcelain, it unites with oxygen, and the oxide fuses with the earthy matters, forming a yellow enamel. When silver leaf or fine wire is intensely heated by galvanism or the oxyhydrogen blowpipe, it burns with greenish-white scintillations, which are very vivid.

The only pure acids which act on silver are the sulphuric and nitric. Both of them oxidize the silver at the expense of their own oxygen, and afterwards dissolve it in the remaining undecomposed acid. Nitric acid is its proper solvent.

The specific gravity of fused silver is 10.47, and after con-

densation under the hammer or press, it is 10.51. It fuses at a bright red heat approaching whiteness, which has been variously stated at 1,280°, 1,860°, and 1,873° of Fahrenheit's thermometer. The latter number is probably the nearest to the truth. Its tenacity is intermediate between that of gold and platinum. Sickingen's numbers for the tenacity of these three metals, are, for gold, 15, for silver, 19, and for platinum, 26¼.

The symbol of silver is Ag, its combining number 1351.607 on the oxygen, and 108.306 on the hydrogen scale.

Suboxide of Silver, Ag_2O. 224.3.—Wöhler obtained the citrate of this oxide by exposing citrate of silver to the action of hydrogen gas at the temperature of 212° F., one-half the oxygen being liberated, and the citric acid combining with the remaining suboxide. Faraday obtains it by exposing an ammoniacal solution of the oxide to the action of the air, when the suboxide falls. When its solution is heated, it deposits metallic silver.

Oxide of Silver, AgO. 116.3.—This oxide is prepared by precipitating a solution of nitrate of silver with pure potassa or baryta, washing thoroughly and drying at a gentle heat. It is a brown powder, anhydrous, becoming black, with loss of oxygen on exposure to the sun. Its specific gravity is 7.143. It is slightly soluble in water, communicating to it a metallic taste and an alkaline reaction. It is easily reduced by heat alone, or by hydrogen at 212° Fahrenheit.

Oxide of silver is a strong base, and forms salts with most of the acids. These salts are colorless unless the acid has a decided tint; they have a styptic metallic taste, and are poisonous. The nitrate and some others are soluble, but most of them dissolve only partially or not at all in water, but readily in ammonia. The metal is thrown down from these solutions by zinc, cadmium, lead, tin, copper, bismuth, mercury, iron, tellurium, antimony, arsenic, phosphorus, phosphorous acid, phosphuretted hydrogen, copperas, tin salt, and many organic bodies. When mercury is employed for this purpose, the silver is deposited in a beautiful arborescence, known as the *Arbor Dianæ*. It always contains mercury. Hydrochloric acid and the chlorides throw down insoluble chloride of silver, and constitute an exceedingly delicate test for the metal, rendering opalescent a solution which

contains but one part of silver in 300,000. Hydriodic and hydrobromic acids throw down a yellowish iodide or bromide from strong solutions. Sulphuretted hydrogen and alkaline sulphurets precipitate a brownish-black sulphuret, soluble in strong nitric acid. Potassa and soda throw down a gray oxide. Ammonia gives the same precipitate and redissolves it in excess. The carbonates produce a white precipitate. The precipitates from arsenites and phosphates are yellow; those from pyrophosphates and metaphosphates, white; from chromates and arseniates, brownish-red or dark-crimson; from cyanides, sulphocyanides, ferrocyanide of potassium, and oxalic acid, white; from ferridcyanide of potassium, reddish-brown. A solution of oxide of silver in ammonia gradually deposits suboxide, AgO_2.

Fulminating Silver.—This appears to be a compound of oxide of silver with ammonia. It is formed by precipitating oxide of silver with lime-water, washing it on a filter, and then spreading it on bibulous paper, to absorb moisture from it. When nearly dry, water of ammonia is poured upon it, and allowed to stand on it for ten or twelve hours, at the end of which period most of the originally precipitated oxide has disappeared, having been dissolved in the ammonia. There remains, however, a black powder, which is carefully removed and spread out upon several pieces of bibulous paper to dry. It may be obtained more expeditiously by dissolving the nitrate of silver in ammonia and precipitating by caustic potash.

This is a terribly explosive compound. When pressed by a hard body, while still moist, it detonates with great violence. In its dry state it is still more dangerous. Heat, electricity, touch, even the agitation of the powder induced by pouring it out, or by stirring it with a feather, produce explosion. Many persons have been seriously injured by it; some have been killed. Nor have these accidents been confined to the inexperienced alone. Professor Hare, of the University of Pennsylvania, was severely wounded by the explosion of a quantity of this substance, whilst he was pouring it upon the head of a hammer, to exhibit its properties to his class. It ought always to be made in small quantities, and kept in little paper boxes, with pasteboard covers laid loosely on them. It should never be kept in

a glass bottle, because, let the precautions observed be what they may, small fragments of the powder are apt to adhere to the neck in pouring it out, and then the introduction of the stopple is followed by an explosion. Nay, more, it is liable to explode from the slight friction produced by the passage of the particles over the glass during the act of pouring it out, and serious accidents have occurred from the jarring of the shelves in which it is kept by the motion of a passing cart. The solution deposits black crystalline particles, which are even more explosive, detonating by simple agitation of the liquid.

Peroxide of Silver.—When a voltaic current is passed through a weak solution of nitrate of silver, needles of a metallic lustre, interlacing with one another, are deposited at the positive pole. When thrown into hydrochloric acid, it causes disengagement of chlorine at the same time that chloride of silver falls. Projected into ammonia, a rapid evolution of nitrogen gas, attended with a hissing sound, takes place, so that the whole liquid froths. A little of the oxide, mixed with phosphorus, and struck with a hammer, detonates. With heat it decrepitates, and becomes metallic silver.

Sulphuret of Silver, AgS. 124.1.—This compound of silver is found native as *silver glance* or *vitreous silver*. It may be made by simply fusing the elements together, or by precipitating a solution of silver with sulphuretted hydrogen or by alkaline sulphuret. It is spontaneously formed whenever silver is brought in contact with a sulphuret, either gaseous or liquid. So strong is the affinity of this metal and sulphur, that it has been used as a convenient blowpipe test for the presence of sulphuric acid. The suspected sulphate is fused with soda and charcoal in the reducing flame. This process gives rise to a sulphuret of sodium, which is soluble in water. The fused bead removed and laid on a bright silver surface, as the face of a coin, is then wet with pure water, allowed to remain a moment in contact with the metallic surface, and then washed away. A dark spot of sulphuret of silver remains on the metal. It has already been said that the air of cities, which contains sulphuretted hydrogen, tarnishes silver. It is well known, also, that a spoon of this metal becomes speedily blackened in contact with eggs or mus-

tard, on account of the sulphur present in those substances. This tarnish is removed with great facility by the use of *chameleon mineral*, made by fusing peroxide of manganese with nitrate of potassa.

Sulphuret of silver is dark brown, soft enough to be cut with a knife, and slightly malleable. Calcination decomposes it, driving off the sulphur, as sulphurous acid, the metallic silver remaining. Nitric acid decomposes it, the resulting compound being nitrate of silver and sulphuric acid, while free sulphur floats in the solution. Sulphuret of silver is a powerful sulphobase, since, though heated to redness, it retains the volatile sulphurets, which are usually driven off from their other combinations at that temperature. The percentage of the elements constituting this compound has been stated at—silver, 87.04; sulphur, 12.96; by calculation, silver 88.51, sulphur 11.49.

Carburets of Silver.—When silver is ignited with lampblack, Ag_2C is formed. Strong ignition of cyanide of silver produces AgC. Pyroracemate of silver, heated for a long time in a water-bath and distilled, yields AgC_2.

Phosphuret of Silver.—This compound may be formed by igniting silver and phosphorus together in a closed crucible. Ignition of the phosphate of silver with charcoal produces the same substance. It is white, granular, sectile, and brittle.

Siliciuret of Silver.—This is a combination of silver with silicon, and is formed by heating under an alkaline glass flux, a mixture of silver powder, charcoal, and silicic acid.

ALLOYS OF SILVER.

Antimony, arsenic, bismuth, zinc, and tin, form brittle alloys with silver. The latter metal, in very small quantity, destroys the ductility of silver. An easy method of separating these two metals is to laminate the alloy in thin plates and distil it with corrosive sublimate. The volatile bichloride of tin passes over and condenses in the receiver. They may also be separated in the humid way.

Manganese and silver form an alloy. Silver and lead unite in all proportions, and are easily separated by cupellation. Iron

and silver fuse together and form an alloy which cannot be resolved by cupellation, but which is easily decomposed by solution in nitric acid and precipitation with hydrochloric acid, or a soluble chloride. The silver may also be separated from this combination by fusion with borax or saltpetre. Steel combines with silver, forming a very hard alloy, silver-steel, which, after heating, contains 1 part of silver in 500. Silver alloys with the precious metals, the malleability of which it diminishes, except in the case of gold and iridium.

Most of the silver of commerce is alloyed with a very minute portion of gold, and Pettenkofer asserts that all the commercial metal which has not been submitted to chemical purification, contains platinum also.

An alloy of silver with one-tenth or one-twelfth of copper, is the standard of coin in most countries. It is harder and more durable than silver alone. When boiled with a solution of cream of tartar and common salt, or when scrubbed with water of ammonia, the superficial particles of copper are removed, and a surface of pure silver is left. A combination of 95 parts of silver to 5 of copper constitutes the metal for medals and for the finest silver plate. Silver solder is composed of different proportions of materials, according as it is designed for the finest or for common work. That used with 95 per cent. silver is composed of silver, 66.6; copper, 23.4; zinc, 10. The common silver solder is made of silver, 66.6; copper, 30; brass, 3.4. The last ingredient renders it an uncertain compound; for, independently of the fact that this is an alloy of no definite proportions, brass always loses zinc, and becomes richer in copper after every fusion.

The following table of silver coin is taken from the same source whence we derived our table of gold coin:—

Table of Silver Coins.

Nation.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
Argentine Republic.				
Dollar of Rio de la Plata,	1828	380	862	88 2
" "	"	411	822	91
" "	"	418	800	90
Half-dollar of Rio de la Plata,	1815	205	888	49
Quarter-dollar of Rio de la Plata,	1813–16	98	886	23 4
Dollar of Argentine Republic,	1838–39	388	928	97
" "	"	427	894	1 02 8
" "	"	412	915	1 01 5
The extreme irregularity of the coinage of this republic, and of the old Spanish province of Rio de la Plata, and its variations in the same year, as seen by the above table, render it impossible to estimate its value in any way but by direct analysis.				
Austria.				
Rix dollar of Maria Theresa,	1753–80	430	835	96 7
" of Joseph II.,	1780–89	431	835	97
" of Leopold II. and Francis I.,	1790–1800	432	835	97 2
" " "	1834	432	833	97
Rix and kremnitz dollar of Ferdinand I.,	1839–40	432.5	834	97 2
Florin of Joseph II.,	1788	215	835	48 4
" of Francis I.,	1834	216	838	48 8
" and kremnitz florin of Ferdinand I.,	1839–40	216.5	834	48 7
Brabant crown of Francis I.,	1793–99	454	875	1 07
20 kreutzer of Francis I.,	1834	103	580	16 1
" of Ferdinand I.,	1840	103	582	16 2
10 kreutzer,		60.5	500	08 1
Scudo of Ferdinand I.,	1839	401.5	902	97 6
Lira,		67	900	16 2
Quarter-lira,		25	606	04 1
Baden.				
Specie dollar of Charles Frederick, Margrave,	1765–78	428	833	96 1
Crown of Interregnum,	1813–16	455	875	1 07 3
" of Louis, Grand Duke,	1819–29	455	877	1 07 5
" of Leopold,	1831–34	456	837	1 07 7
Two guilder of Louis, Grand Duke,	1822–25	392	755	79 8
Guilder of Leopold,	1837–39	164	900	39 7
Bavaria.				
Specie dollar of Maximilian Joseph and Charles Theodore,	1755–1810	430	833	96 5
Specie dollar of King Maximilian,		430	835	96 7
Crown (palatinate) of Charles Theodore,		397	995	1 06 4
" of Kings Maximilian and Louis,	1809–32	455	875	1 07 2
Florin (palatinate),	1758	198	995	53 1
" of King Louis,	1839	163.5	900	39 6
Six kreutzers of King Louis,	1833	41	320	03 5

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
BELGIUM.				
Crown of Joseph II. and Leopold II.,	1781–92	453	875	1 06 7
" of Francis II.,	1793–1800	454	878	1 07
Five francs of Leopold I.,	1833–35	385.5	895	93 1
Franc of Leopold I.,	1833–35	77	897	18 6
Two francs same fineness as five francs; fractions like the franc.				
BOLIVIA.				
Dollar,	1827–37	416.5	902	1 01 2
"	1840	417	900	1 01
Half-dollar,	1827–28	208	903	50 5
"	1830	208	670	37 5
Quarter-dollar,	1827–28	104	900	25 2
"	1830	103.5	675	18 8
BRAZIL.				
640 reis of Joseph I.,	1750–77	274	915	67 5
" of Maria I. and Peter III.,	1777–86	267	903	64 9
" of Maria I.,	1786–87	274	903	66 6
" "	1800–04	294	903	71 4
" of John, Regent,	1804–16	284	903	69
" of John VI.,	1816–21	275	910	67 4
" of Peter I.,	1822–26	276	905	67 2
320 reis of John, Regent,	1804–16	132	910	32 3
1200 reis of Peter II.,	1837	414	891	99 4
800 " "	1838	276	891	66 2
400 " "	1837	138	886	33
The other coins of the same dates are of the same fineness.				
BRITAIN.				
Shilling of George I.,	1721–23	87	930	21 8
" of George II.,	1727–46	90	930	22 5
" of George III.,	1787	92	926	22 9
" "	1816–17	86	934	21 6
" of George IV.,	1820–29	86.5	930	21 7
" of William IV.,	1831	87	930	21 8
" Victoria,	1838–40	87	925	21 7
Crown of George IV.,	1822	435	930	1 07
The other pieces are proportional, the fineness being the same for the same date. The bank tokens are dollars restamped.				
BRUNSWICK.				
Florin of Anthony Ulrich,	1704	201	997	54
" (Leipzig) of Charles,	1764	198	997	53 2
" of Charles William Ferdinand,	1789–1800	263	750	53 1
Specie thaler of Charles and Charles William Ferdinand,	1764–90	428	833	96
Thaler of William,	1838	343	750	69 3
$\frac{1}{6}$ thaler of Charles,	1764–75	78	564	11 8
" of Charles William Ferdinand,	1780–92	78.5	561	11 9

Table of Silver Coins—*Continued.*

Nation.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
Central America.				
Dollar,	1824–36	415	899	1 00 1
Chili.				
Dollar,		414	907	1 01
The coinage of the last two countries are averaged. The standard of the Chilian dollar ranges from 905 to 911 thousandths.				
Colombia.				
Dollar of eight reals,	1819–21	363*	730	71 4
" " of Bogota,	1835–36	417†	910	1 02 2
" " of New Granada,	1839	356	680	65 2
2 reals of Caraccas and Cundinamarca,	1815–21	74	690	13 8
¼ Real of Caraccas,	1829–30	8.5	795	01 8
Denmark.				
Specie daler of Christian VII.,	1769–77	444	875	1 04 6
" of Frederick VI.,		445	877	1 05 1
60 schillings Holstein of Christian VII.,	1787–94	444	878	1 05
40 " or two-thirds, of Christian VII.,	1787–97	295	878	69 8
10 " of Christian VII.,	1787–89	93	670	16 8
⅛ specie daler of Christian VIII.,	1798–1801	113	670	20 8
Rigsbank daler of Frederick VI.,	1813–39	222.5	877	52 6
32 skillings of Frederick VI.,	1820	93.5	692	17 4
Egypt.				
The first date given for these coins is the year of the Hegira, the second the Christian era.				
Yismilik, or ½ piastre, of Selim III.,	1216 (1801)	96	372	09 6
Real, or 20 piastres of Abdul Majeed,	1255 (1839)	430	836	96 8
Nasf, or 10 piastres, of Abdul Majeed,	1255 (1839)	215	832	48 2
Ruba, or 5 piastres, of Mahmoud II.,	1252 (1836)	107.5	850	24 6
Ghersh, or piastre, of Abdul Majeed,	1255 (1839)	21	842	04 8
Ashreena, or 20 paras, of Abdul Majeed,	1255 (1839)	10.5	843	02 4
France.				
Crown of Louis XV.,	1726–73	440	912	1 08 1
" of Louis XVI.,	1774–92	444	912	1 09 1
Half-crown of Louis XV.,	1726–73	212	912	52 1
" of Louis XVI.,	1774–92	220	912	54
Thirty sols of Louis XVI.,	1792	153	667	27 5
Fifteen sols of Louis XVI.,	1792	77	662	13 7
Six livres of Louis XVI.,	1793	445	912	1 09 3
Five francs of year IV. of Republic, and Bonaparte, 1st Consul,	1803–04	383	902	93 1
" of Napoleon, Emperor,	1804–14	383.5	902	93 2
" of Louis XVIII.,	1815–24	384	902	93 3
" of Charles X.,	1825–30	384.5	902	93 4
" of Louis Philippe,	1831 and seq.	385	899	93 2
The standard of the smaller French coins since the commencement of Louis Philippe's reign, when the humid assay of silver, invented by Gay-Lussac, was introduced into the French mints, has been 900.				

* Varies from 849 to 854 in fineness, and from 343 to 382 in weight.
† Varies in fineness from 907 to 917.

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
GREECE.				
Five drachm of Otho,	1833	345	900	83 6
Drachmé of Otho,	1832–33	68.5	902	16 6
GUIANA (BRITISH).				
Dollar of three guilders of George III.,	1809	359	824	79 7
Guilder of George III.,	1816	119	825	26 4
" of William IV.,	1832	119.5	819	26 4
HANOVER.				
Specie thaler of George III.,	1766	449	896	1 08 3
Florin of George III.,	1783–97 and 1807–14	201	995	53 9
" "	1801	266	753	54
" of George IV.,	1825	202	996	54 2
HESSE CASSEL.				
Specie thaler of Frederic II.,	1766	430	836	96 8
Thaler of Frederic II.,	1778	360	750	72 7
" of William IX.,	1789	291	885	69 4
" of William II. and Frederick William,	1832–37	341.5	748	68 8
$\frac{1}{3}$ thaler of William II.,	1824–27	130.5	660	23 2
$\frac{1}{6}$ thaler of William II.,	1823–30	81	505	11
" of William II. and Frederick William,	1833–36	82	525	11 6
HESSE DARMSTADT.				
Specie thaler of Louis I.,	1809	432	833	96 9
Crown of Louis I.,	1825	455	875	1 07 2
Gulden of Louis II.,	1838–39	164	900	39 8
Two thalers of Louis II.,	1839	574	900	1 39 1
HINDOSTAN.				
Sicca rupee of Mogul Empire, Shah Alum,		177	938	44 7
" " Arcot,	1782	177	958	45 7
" of Bengal, 19th sun,		179	980	47 2
" "	1818	192	920	47 6
Rupee of Bombay,	1818	179	920	44 4
"	1818–40	180	917	44 5
Quarter-pagoda of Madras,		164	900	39 8
Double-fanam of Southern India,		28	909	06 9
Fanam of Southern India,		14	920	03 5
MALAY ARCHIPELAGO.				
Silver rupee of Dutch government of Java,	1783	200	833	45
" " "	1796	200	663	35 7
Guilder of Dutch government,	1820	166	898	40 2
" "	1839	155	944	39 4
Ducatoon of Dutch government,	1766–1804	500	938	1 26 3
Half-guilder of Dutch government,	1826	83	898	20 1
Quarter-guilder of Dutch government,	1840	62.5	569	09 6
MAURITIUS.				
Ten livres,	1810	414	833	92 5

Table of Silver Coins—*Continued.*

Nation.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
Mecklenburg Schwerin.				
Florin of Frederick Francis,	1790–1808	265	753	53 7
" of Paul Frederick,	1839 and seq.	203.5	988	54 1
Eight schilling of Frederick Francis,	1827	103	440	12 2
Mexico.				
Dollar of Mexico, Augustin, Emperor,	1822–23	416	898	1 00 6
" of Mexican Republic,	1830–34	416	901	1 01
" " "	1835	416	906	1 01 5
" " "	1836	416.5	904	1 01 4
" " "	1837	416.5	903	1 01 3
" " "	1840–41	416.5	902	1 01 2
" of Zacatecas,	1834–35	415.5	896	1 00 3
" "	1836	416.5	898	1 00 7
" "	1837	408	895	98 4
" "	1840	414	895	99 8
" "	1841	414	897	1 00
" of Guanaxuato,	1832–35	416	894	1 00 2
" "	1837	412.5	900	1 00
" "	1838	417	901	1 01 2
" "	1840–41	417	896	1 00 7
" of Durango,	1833–34	415	904	1 01 1
" "	1837–39	417	902	1 01 3
" of Potosi,	1835	417	902	1 01 3
" "	1837–41	416.5	901	1 01 1
" of Chihuahua,	1833	417	899	1 01 1
" "	1840–41	420	907	1 02 6
" of Guadalaxara,	1832	416.5	883	99 1
" "	1835	416	870	94 2
" "	1835	416.8	884	97 5
" "	1835	416.5	895	99 2
" "	1840	417	904	1 00 4
Hammered dollar,	1811–18	404	880	95 4
Cast dollar,		417	916	1 03
Vargas dollar,	1811–12	405	890	97 1
Morelos dollar,	1812–13	407	880	96 4
Half-dollar of Mexico,	1827	207	905	50 4
" of Zacatecas,	1831–36	206	898	49 8
" of Guanaxuato,	1835–38	206	901	50
Quarter-dollar of Mexico,	1825–28	102.5	902	25
" " *agachado*,	1824	101	898	24 4
" "	1824	100	900	24 2
" "	1832–34	103	893	24 6
" of Zacatecas,	1825–30	103	897	24 7
" "	1832–35	105	898	25 4
Milan.				
Scudo, six liras, of Maria Theresa,	1778	352	898	85 1
" " of Ferdinand I.,	1839	401.5	902	97 6
Lira of Maria Theresa,	1780	95	550	14 1
" of Ferdinand I.,	1809	67	900	16 2
" of Napoleon,	1805–14	76	902	18 5
Quarter-lira of Francis I.,	1822	24.5	590	03 9
" of Ferdinand I.,	1839	25	606	04 1

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
NAPLES AND SICILY.				
Scudo of Ferdinand IV.,	1783	390	900	94 5
" "	1786–98	422	835	94 9
" of Ferdinand IV. and Mary Caroline,	1791	422	842	95 7
" of Sicily, Ferdinand,	1785–99	419	830	93 7
" of Republic and Joseph Napoleon,	1799–1805	422	835	94 9
" of Sicily, Ferdinand III.,	1810	420	835	94 5
" of Ferdinand II.,	1831–33	426	830	95
Silver ducat of Ferdinand IV.,	1784–85	348	842	78 9
Carlin of Ferdinand IV.,	1791–95	34	835	7 6
Lira of Joachim Napoleon,	1810	76	900	18 5
NETHERLANDS.				
Ducatoon of William V., Stadtholder,	1766–95	500	938	1 26 3
Rix dollar " "	"	428	872	1 00 5
" of Louis Napoleon,	1806	436	881	1 03 5
" "	1808	408	912	1 00 2
Guilder of William V.,	1766–95	161	912	39 5
" of Batavian Republic,	1796–1805	157	904	38 2
" of William I.,	1816–38	166	896	40 1
25 cents of William I.,	1824–30	65	569	10
PERSIA.				
Hazar-dinar of Fatha Ali,		106	952	27 1
Sahib-koran of Fatha Ali,	1222 (1807)	159	945	40 4
PERU.				
Dollar of Lima,	1822–35	416	901	1 01
" "	1837–38	415	904	1 01
" "	1841	415	899	1 00 5
" of Cuzco,	1837–38	414	904	1 00 8
Half-dollar of Cuzco,	1835	208	650	36 4
" "	1836	207	667	37 2
" of Arequipa,	1838	206	660	36 6
Quarter-dollar of Lima,	1828–32	105	900	25 4
" of Cuzco,	1827	105	902	25 5
" "	1835	102	654	18
POLAND.				
Convention thaler of Stanislaus Augustus,	1784	430	833	96 5
Thaler of Stanislaus Augustus,	1794	370	688	68 6
Zloty of Nicholas I.,	1838	48	872	11 3
PORTUGAL.				
Cruzado of Maria I. and John VI.,	1795–1826	222	900	53 8
" of Maria II.,	1833	226	908	55 3
12 macutas of Maria I. (African colonies),	1789	271	896	65 4
Crown of 1000 reis of Maria II.,	1838	456	912	1 12
Piece of 200 reis of Maria II.,	1838	91	920	22 6
6 vintems of Maria II.,	1833	55	898	13 3

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
PRUSSIA.				
Thaler of Frederick II.,	1750	338	754	68 6
" "	1764–86	340	750	68 7
" of Frederick William II.,	1789–96	340	749	68 6
" of Frederick William III.,	1798–1803	340.5	745	68 3
" " "	1813–19	341	748	68 7
" " "	1823–31	343	750	69 3
Convention thaler of Frederick William II. (for Brandenburg),	1795	430	830	96 1
$\frac{2}{3}$ piece of Fred. William II. (for Brandenburg),	1797	265	750	53 5
$\frac{1}{3}$ thaler of Frederick II.,	1768–86	126	668	22 7
" of Frederick William II.,	1786–97	126	670	22 7
" of Frederick William III.,	1809	126	667	22 6
$\frac{1}{6}$ thaler of Frederick II.,	1764–73	78	519	10 9
" Frederick William II.,	1796–97	80	515	11 1
" Frederick William III.,	1801–18	80.5	517	11 2
" " "	1822–28	81.5	526	11 5
ROME.				
Scudo of Pius VI.,		408	913	1 00 4
" of Republic,	1799	408	899	98 8
" of Senate of Bologna,	1797	456	842	1 03 4
" of Pius VII.,	1800–02	408	913	1 00 4
" "	1815	408.5	925	1 01 8
" of Gregory XVI.,	1835	415	900	1 00 6
Testoon of Pius VI.,	1796	120.5	913	29 6
" of *sede vacante*,	1830	122	925	30 4
RUSSIA.				
Rouble of Peter the Great,	1724	432	729	84 8
" of Catharine I.,	1725	418	736	82 9
" of Elizabeth,	1750	398	792	84 9
" of Catharine II.,	1775	360	757	73 4
" of Paul I.,	1799	323	870	75 7
" of Alexander I.,	1801–14	318	875	75
" of Nicholas,	1837 and seq.	320	875	75 4
10 zlots of Nicholas,	1835	486	871	1 14
20 copecks of Alexander I.,	1802	62	875	14 6
" "	1810	72	760	14 7
" "	1813	63	877	14 9
" of Nicholas,	1837 and seq.	65	875	15 3
30 copecks of Nicholas,	1838	94	872	22 1
SARDINIA.				
Scudo of Victor Amadeus,	1773	540	906	1 21 8
" " (island),	1773	361	896	87 1
" of Republic of Genoa,	1796	512	889	1 22 6
" of Ligurian Republic,	1798	512	885	1 22
Five francs of Republic,	1800	384	892	92 3
Five lire,		385	902	93 5
Lira of Republic of Genoa,	1794	62	889	14 8

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
SAXONY.				
Specie thaler of Frederick Augustus II.,	1763	428	842	97 1
" of Frederick Christian,	1763	430	839	97 2
"	1764–1816	432	835	97 1
"	1818–36	430	834	96 6
" of Gross-herzog Sachsen (Weimar),	1815	477	755	97
Half-specie thaler of Fred. Augustus III.,	1813–26	214	833	48
Quarter-specie thaler of Fred. Augustus III.,	1800–02	107	838	24 2
Sixth-specie thaler of Fred. Augustus III.,	1803–10	83	537	12
New thaler of Frederick Augustus IV.,	1839	344	750	69 5
SPAIN.				
Cob dollar of Philip V. & Charles III. Amer.,	1736–70	410	915*	1 01
Dollar of Philip V. & Charles III., Spanish,	1731–32	410	910	1 00 6
Globe dollar of Philip V. & Charles III., Amer.,	1736–71	411	910	1 00 8
Dollar of Charles III., Spanish,	1772–88	412	900	99 8
" of Ferdinand VII., Spanish,	1808–21	414	900	1 00 4
Pillar dollar of Charles III. & IV., Amer.,	1772–1808	413	898†	99 8
" of Ferdinand VII., American,‡	1808–25	414	898	1 00 1
Pistareen of Charles the Pretender,	1707–12	70	900	17
" of Philip V.,	1715–37	81	833	18 2
" of Charles III.,	1759–71	85	826	18 9
" "	1772–1808	85	813	18 6
" of Isabella II.,	1835–37	90.5	810	19 7
Five pesetas of Barcelona coinage,	1809–11	404	896	97 5
Ten reals of *Resellado*,	1821	208	920	51 5
SWEDEN.				
Specie daler of Gustavus III. and IV.,	1771–1801	449	880	1 06 5
" of Charles John XIV.,	1830–38	525	751	1 06 2
$\frac{1}{3}$ specie daler of Gustavus III.,	1784	147	875	34 6
$\frac{1}{6}$ specie daler of Gustavus IV.,	1803–07	95	686	17 6
SWITZERLAND.				
Ecu of Zurich,	1790–94	390	844	88 7
" of forty batzen of Berne,	1795–98	452	903	1 10
" of three livres (Genevoise) of Geneva,	1796	464	868	1 08 5
Franken of Berne,	1797	122	833	27 4
Four franken of Helvetian Republic,	1801	452	900	1 09 6
Ten batzen of Lucerne,	1812	110	904	26 8
" of Vaud,	1823	112	900	27 1
Five batzen of Berne,	1826	67	760	13
" of Vaud,	1813	63	666	11 3
Thaler of Basle,	1763	356	833	80
Crown of Basle,	1795	412	840	93 2
TRIPOLI.				
Ghersh of 100 paras of Mahmoud II.,		188	354	17 9
" " of Youssouf Pasha,		153	244	10
Half-ghersh of 100 paras of Mahmoud II.,		98	306	8 1
" " of Youssouf Pasha,		78	241	5 1
Utchlik of Nedgib Pasha,		227	245	15

* Varies from 913 to 922. † Varies from 897 to 903.
‡ After 1821 they were struck at Madrid The fineness sometimes is as high as 905.

TABLE OF SILVER COINS—*Continued.*

NATION.		Weight.	Fineness.	Value.
		Grains.	Thous.	d. c. m.
TUNIS.				
Piastre of Abdul Hamed, Sultan,		238	408	26 1
" of Mahmoud II.,		176	263	12 8
Double piastre of Mahmoud II.,		358	270	26
TURKEY.				
Ghersh, or piastre, of Abdul Hamid,	1773	294	500	39 6
" " "	1783	284	550	42 1
" " of Selim III.,	1794–1801	200	486	26 2
" " of Mahmoud II.,	1823	94	470	11 9
Altmicklik, 1½ piastre, of Abdul Hamid,	1784	410	550	60 7
Para of Selim III..	1794	5	500	7
" of Abdul Medjid,	1840	2	77	⅓
TUSCANY.				
Francescone of Francis III.,	1740–65	419	920	1 03 8
Half-francescone of Francis III.,	1740–65	199	918	49
Ten pauls of Ferdinand III.,	1791–1801	419	920	1 03 8
" "	1803–07	420	917	1 03 7
" "	1814–24	421	920	1 04 3
Ten livres of Charles I. and Maria Louisa,	1803–07	607	962	1 57 3
UNITED STATES.				
Dollar,	1792–1837	416	892.4	99 9
"	1837 and seq.	412½	900	1 00
The silver coinage of the present year (1853) is debased in order to bring it down to a standard which will prevent it from leaving the country, and which will meet the rise in price of this metal, resulting from the changed relations between it and gold, which have arisen from the increased quantity of the latter recently thrown into the market.*				
WURTEMBERG.				
Convention thaler of Charles,	1760–84	428	836	96 4
" of Frederick,	1806	430	833	96 5
Crown of William,	1818–33	454	875	1 07
Gulden of William,	1824	195	750	39 4

In the above table, as well as in that of gold coins, the fractions of coins are not contained when they are of the same fineness as the units. So, too, slight deviations in weight in the same coin are not taken into account when the fineness remains unchanged.

Silver plate is a variable alloy. That of England is stamped, and has a uniform fineness of 925 thousandths. The stamp is

* The three cent piece contains 3 parts of silver to 2 of copper.

a *lion*, with the initials of the maker's name, the seal of the assay office at which the plate was examined, and a letter for the date. The mark of the goldsmith's office is a leopard's head; the office at Dublin, a harp; at Edinburgh, a thistle; at Sheffield, a crown; at Birmingham, an anchor; at Newcastle, three castles. The letter, used by the Goldsmiths' Company, shows the date by beginning the alphabet at 1817. In France there are two standards, 950 and 800 thousandths. The Austrian standard is 900. Prussia has no standard, but the Corporation of Goldsmiths controls the manufacture of plate, so as to bring it to 750. The Mexican rate is 917, though it is not compulsory. In the United States there is no law establishing the quality of plate. It is, however, usually that of our coin, from which most of it is manufactured.

SALTS OF SILVER.

HALOID SALTS.

Chloride of Silver, AgCl. 143.42.—This substance, which occurs native as *horn silver*, contains 75.33 per cent. of silver, and is formed, as already described, by adding hydrochloric acid, or any soluble chloride, to a solution of the metal. A white, curdy precipitate falls, which is to be washed and dried away from the light. Heated to dull redness, it fuses to a clear yellow liquid, which is converted, on cooling, into a semitransparent, gray, or colorless solid, so soft as to receive an impression from the nail.

Fusion with potassa, or a stream of hydrogen, as already described, reduces it to a metallic state. Mohr says the best way of reducing it is to mix it with one-third its weight of colophony (black rosin), and to heat the mixture moderately in a crucible, till the flame ceases to be of a greenish-blue color; then suddenly to increase the fire so as to melt the metal into an ingot. Zinc, tin, cadmium, bismuth, copper, lead, mercury, arsenic, and antimony reduce it under water. It is not decomposed at a red heat, even when mixed with calcined charcoal; but hydrogen or steam, passed over the fused chloride, drives off chlorine as hydrochloric acid, and leaves metallic silver.

Alkaline solutions do not decompose it, but it forms double salts with the alkaline chlorides by boiling them together, and the compound salt separates in crystals on cooling. A new method of obtaining silver from its ores, based upon this property of its chloride, has been suggested. The ore is roasted with common salt to form chloride of silver, which is dissolved out by means of a hot solution of salt. The silver is precipitated by metallic copper. Cyanide of potassium also dissolves it, and it crystallizes out of the solution, on evaporation. It is insoluble in water, very soluble in water of ammonia, crystallizing out of its solution.

Subchloride of Silver, Ag_2Cl.—When the last described compound of silver is placed in the direct rays of the sun, under water, hydrochloric acid is evolved, and the precipitate changes to a blue-black. The same result takes place, but with less rapidity, when the diffused light of a room is allowed to act upon the precipitated chloride. Berthollet regarded this color as due to the formation of the oxide of silver. It is now generally conceded, however, that a new and definite compound of chlorine and silver has been formed. The same substance may be obtained by pouring a solution of deuto-chloride of copper or perchloride of iron upon silver leaf. The metal is speedily altered to black spangles, which, being quickly washed and dried, constitute the subchloride of silver. Should the solution remain too long in contact with the silver, the chloride will be formed. Hydrochloric acid, acting on suboxide of silver, gives rise to the same compound. It is a brownish or black powder, with metallic streak, which, when heated to the fusing point of chloride, is converted into chloride and metallic silver.

Bromide of Silver, AgBr. 186.7.—This is formed, like the chloride, by double decomposition of a salt of silver with a soluble bromide. It is yellow, fusible to a red liquid, which congeals to a translucent soft mass. It is only slightly soluble in dilute ammonia. When disseminated in water, it is easily decomposed by chlorine. It forms double salts with the alkaline bromides.

Iodide of Silver, AgI. 234.6.—Formed like the last two salts, substituting a soluble iodide. It is of a greenish yellow

color; fuses to a red liquid, which congeals to a dirty yellow, opaque mass; is readily decomposed by chlorine when heated; is soluble in strong solutions of iodide of potassium, and chloride of potassium or sodium; is scarcely soluble in ammonia. It forms double salts with alkaline iodides, with cyanide of potassium and with basic nitrate of mercury, forming with the last the compound $AgI + Hgo, No_5 + HO$.

Iodide of silver possesses, in common with other metallic salts, the remarkable property of changing its color with variations of temperature. If a sheet of white paper be washed over with a solution of nitrate of silver, and afterwards with iodide of potassium, it immediately assumes the pale primrose yellow tint of the cold iodide of silver. On gently heating the paper, the gaudy brilliance of the sunflower takes the place of the paler yellow, into which it gradually fades as the paper cools. These changes may be continued indefinitely, provided too high a heat be avoided. Pressing the finger upon the warm paper produces a white spot, by suddenly cooling the part with which it comes in contact.

Fluoride of Silver, AgFl. 127.05.—This soluble salt is formed by the action of hydrofluoric acid on carbonate of silver. When dry, it is fusible, like the chloride.

Silico-fluoride ($3AgF + 2SiF_3$) is soluble and crystallizable, and is precipitated as a basic salt by ammonia.

OXYSALTS.

Sulphate of Silver, AgO,SO_3. 156.4.—Sulphate of silver may be prepared by the action of boiling sulphuric acid on the metal, as described under the head of parting gold and silver by means of this acid. It may also be procured by dissolving the oxide or carbonate in dilute oil of vitriol. It is soluble in nitric acid, from which solution it crystallizes in white shining crystals; is isomorphic with dry sulphate of soda. It is dissolved in 88 parts of boiling water, but, on cooling, the greater part falls down in acicular crystals. Dissolved in ammonia, it crystallizes out as $AgO,SO_3 + 2NH_3$. Nitric acid converts sulphuret of silver into a brownish-yellow oxysulphate or sulphobasic sulphate of silver.

Sulphite of Silver, AgO,SO_2. 148.4.—This salt is precipitated from a solution of nitrate of silver by sulphuric acid or a sulphite. Hyposulphate or dithionate of silver (AgO,S_2O_5+2Ho), is obtained from a solution of carbonate of silver in dithionic acid.

Hyposulphite of Silver.—Dithionite of silver, AgO,S_2O_2. 172.5. When moderately dilute nitrate of silver is added to a concentrated alkaline dithionite in excess, a gray precipitate falls, which is a mixture of dithionite and sulphate of silver. This is to be well washed with pure water and digested with ammonia, which dissolves the dithionite of silver. It is precipitated from its ammoniacal solution by the careful addition of nitric acid to exact neutralization. It is filtered, and dried rapidly in paper. This salt forms double salts with other dithionites. These are made by saturating a solution of an alkaline dithionite with chloride of silver, and precipitating by alcohol. The precipitate is to be dried in vacuo, over oil of vitriol. Oxide of silver has so powerful an affinity for dithionous acid that it abstracts half of it from alkaline dithionites, making a strongly alkaline solution. The alkaline double salts are crystalline; those of strontia, lime, and lead are white powders. They are all characterized by intense sweetness. The double hyposulphite of silver and ammonia is said to be so extremely sweet as to communicate a sensation of pain to the tongue, and to impart a sweet taste to 32,000 parts of water. Trithionate and tetrathionate of silver are whitish and yellow.

Nitrate of Silver, AgO,NO_5.—This salt is formed directly by the union of pure silver with pure nitric acid; more conveniently, however, by acting upon silver coin with the same acid. A few insoluble dark flocks are left after the action of the acid. These are minute portions of gold, contained in nearly all silver coin, and are to be separated by filtration. The filtered liquid has a pale blue tint, owing to the presence of nitrate of copper. This salt is separated by two different methods from the nitrate of silver. One of these is the evaporation of the solution to dryness and the fusion of the resulting salt in a platinum capsule, till all green tint disappears from the salt, or better, till a portion of it, taken out and dissolved in water, gives no red precipitate

with ferrocyanide of potassium. This process depends upon the ready decomposition of nitrate of copper by heat, and its reduction to oxide of copper. This being insoluble in water, the desired salt is easily obtained pure by solution in water and crystallization. Another method is to precipitate the mixed nitrates by hydrochloric acid, to reduce the chloride of silver by zinc, as already directed, to redissolve in dilute nitric acid, and to crystallize from this solution, or to fuse it and cast it in cylinders. In the latter form, it is called *lapis infernalis*, or *lunar caustic*, and is used largely by surgeons as an escharotic, styptic, and local alterative.

The crystals belong to the right rhombic system. They are colorless and transparent, and do not deliquesce by exposure to the air. They contain no water of crystallization, and fuse readily to a clear liquid, which congeals to a fibrous solid without loss of weight. This salt destroys organic matter, leaving a white pellicle, which turns to a black crust. The pure salt is soluble in its own weight of cold, half its weight of hot water, and in four times its weight of hot alcohol. The aqueous solution in a glass bottle undergoes no change even in sunlight; but when exposed to light, especially to the direct rays of the sun, in contact with paper, or any organic substance, a black stain is quickly produced, owing to the decomposition of the salt and reduction of its oxide. This reaction is so constant and so prompt that it is a most delicate test for the presence of organic matter, and used in medico-legal examinations for the removal of this disturbing element from solutions containing some of the metallic poisons. It deflagrates on redhot coals; and, when mixed with phosphorus, explodes at a blow. At low redness it is decomposed into silver, oxygen, nitrogen, and nitric oxide.

To the analytical chemist, nitrate of silver is an invaluable reagent, being applied to the detection of a variety of substances. By the housewife it is used for marking linen, under the name of indelible ink. The barber makes a solution of it for the purpose of blackening hair of various light tints, which he accomplishes by washing the hair with it and exposing it to light or the action of some soluble sulphuret.

There are a number of double nitrates. The ammonio-nitrate

(AgO,NO_5+2NH_3) crystallizes from a solution of the simple nitrate in ammonia. It darkens readily in the light. It is one of the liquid tests for arsenic, with which it gives a pale-yellow precipitate. The double salt with mercury ($AgO,NO_5+HgONO_5$) is crystallizable. There are also double salts with the cyanides of copper, silver, and mercury.

Nitrite of Silver, AgO,NO_3. 156.3.—When a solution of nitrite of soda is poured into a solution of nitrate of silver, a precipitate subsides, which is soluble in hot water, from which it crystallizes. This nitrite of silver is white, soluble in 120 parts of water at 59°. It may be used to prepare other metallic nitrites by adding it to the chlorides.

The basic salt is formed by boiling silver with nitrate of silver, and evaporating the yellow solution till it thickens on cooling to a crystalline mass. Water decomposes it into a neutral and more basic salt, which separates as a yellow powder.

Phosphate of Silver, $3AgOPO_5$. 187.7.—When a solution of the common phosphate of soda is dropped into a neutral solution of nitrate of silver, a lemon-yellow powder, the phosphate or triphosphate of silver, subsides. It is soluble in acids or ammonia, subsiding from the latter in crystalline grains. It must be dried away from the light, for, like other salts of silver, it blackens when exposed. Its color changes to reddish brown on the application of heat, but, on cooling, returns to its original color again. It fuses at a white heat.

The neutral phosphate is made by dissolving the basic salt in warm, concentrated phosphoric acid, or by adding excess of phosphoric acid to nitrate of silver and evaporating. It forms large colorless crystals, which are decomposed by water, leaving the yellow basic salt.

The *neutral phosphate* of the bibasic acid, the dipyrophosphate of oxide of silver ($2AgO,PO_5$) is obtained by adding dipyrophosphate of soda to nitrate of silver. It falls as a snow-white granular precipitate, which fuses at a heat below incandescence into a dark-brown liquid, becoming, on cooling, a crystalline enamel. The biphosphate of the same group ($AgOPO_5$) is precipitated from nitrate of silver by an ice-cold solution of freshly ignited bibasic phosphoric acid. It is white, very fusible at a

temperature a little above the boiling point of water. It loses acid by washing, and if heated gradually in water to 212°, it forms a sesquiphosphate ($3\ AgO,2PO_5$).

Perchlorate of Silver, AgO,ClO_7. 207.78.—This salt is made by the direct action of perchloric acid on oxide of silver. It is a white powder, deliquescent and soluble in alcohol. It melts and explodes at a heat below redness.

Chlorate of Silver, AgO,ClO_5. 191.78.—This salt, like the last, is made by the direct union of its component parts. It crystallizes in four-sided prisms, which are soluble in 5 parts of cold and 2 parts of hot water, and slightly in alcohol. It is more explosive than the alkaline chlorates, and is decomposed by acids into oxygen and chloride of silver. When ammonia is added in excess to its solution and evaporated, crystals of ammonio-chlorate of the form AgO,ClO_5+2NH_3, separate.

Chlorite of Silver, AgO,ClO_3. 175.78.—This salt occurs in yellow crystalline scales, and is formed by precipitating nitrate of silver with an alkaline chlorite, boiling the precipitate with water, filtering hot and crystallizing. It explodes at 221°.

Basic Periodate of Silver, $2AgO,IO_7+3HO$.—Basic periodate of soda throws down, from a solution of nitrate of silver, a precipitate, which dissolves in warm nitric acid, and separates, on cooling, in shining straw-yellow crystals. It is the basic periodate of silver, which loses its water of crystallization on being treated with warm water, and is converted into a red salt of the formula $3AgO,IO_7+HO$. The salt $AgOIO_7$, in yellow crystals, decomposed by water into the basic salts, separates when the solution in nitric acid is evaporated.

Iodate of Silver, $AgOIO_5$.—This salt is precipitated when an iodate of an alkali is added to nitrate of silver. It is white, and soluble in ammonia.

Carbonate of Silver, AgO,CO_2. 138.3.—This salt precipitates from a solution of silver, on the addition of an alkaline carbonate. It is yellowish, slightly soluble in water. A white ammonio-carbonate is obtained by precipitating its ammoniacal solution with alcohol.

Borate of Silver, AgO,BO_3. 151.1.—A white, fusible, slightly

soluble salt, precipitated when a concentrated solution of borax is mixed with a solution of nitrate of silver.

Chromate of Silver.—A soluble chromate added to a solution throws down a crimson chromate of the metal. If precipitated from acid solutions, a bichromate is formed, which may be obtained by direct action on silver in fine tabular crystals of a rich crimson. The bichromate, when boiled in distilled water, falls down in micaceous crystals, and is partly decomposed into chromic acid and the neutral chromate, which, thus prepared, is green by reflected and crimson by transmitted light, and in powder.

Triarseniate of Silver ($3AgO,As_2O_5$) is a brick-red powder, obtained by precipitating nitrate of silver with an arseniate of soda. It may retain some of the nitrate, a property which it shares in common with the phosphate.

CHAPTER IV.

COPPER.

Copper is a very abundant metal, and was well known to the ancients. With them, indeed, it supplied the place of steel. The tools which have been found in the old Egyptian quarries are made of hardened copper. The weapons of the most ancient times were constructed, as Hesiod informs us, of brass, iron not being yet used for that purpose. The shields, helmets, and swords of Homer's heroes were formed of the same material. In later times, when iron had superseded the ancient metal, the same name, χαλκευς, originally applied to the armorer, and meaning a worker in brass or bronze, was retained as the appellation of the blacksmith who wrought in iron. The brass of the ancients, or χαλκυς, a name derived from the Arabic, and signifying anything capable of being polished, was not the compound to which we apply that name, but a sort of bronze, or alloy of copper and tin. Our English word copper, as well as the terms

used in the different modern languages to designate this metal, are derived from the Latin *cuprum*, which itself comes from Cyprus or Kupros, as it was spelt by the Greeks, an island sacred to Venus, where it was extensively mined and smelted in very ancient times. The alchemical title of copper was Venus, and the symbol of the planet was applied to the metal.

The ores of copper are so numerous that it would be impossible in this place to give anything like a full account of them. A glance at a few of the more prominent and important of these must suffice.

Native copper is found in most mines of the metal, and in some places it is exceedingly abundant. It is occasionally found crystallized in octahedra and allied forms. More commonly, however, it occurs in strings, and dendritic lumps, imbedded in various stones, and in great masses resting on the surface of the earth. Lake Superior is a well-known locality of the metal. The mass lying in front of the War Office, at Washington, which came from that region, is supposed to weigh nearly a ton. Much of the copper sent to the Eastern States from the mines on Lake Superior is in great slabs, often over an inch in thickness. In Virginia, it abounds in the Epidotic trap of the Blue Ridge, much of that rock being minutely penetrated by the metal, its exposed surface being covered, and its narrow crevices filled with sheets of copper. At the Manassas Gap, regular veins of igneous rock are worked, which are full of native copper and the oxides.

Copper pyrites is one of the most valuable and abundant of the ores of this metal. It occurs in crystals belonging to the quadratic system. These are a definite compound. Rose's analysis of them gives in percentage, sulphur, 35.87; copper, 34.40; iron, 30.47; gangue, 0.27, with a gain of 1.01. Another analysis by the same hand amounted to copper, 33.12; iron, 30; sulphur, 36.52; silica, 39, with an excess of 0.3. Berthier found copper, 32.1; iron, 31.5; sulphur, 36.3; loss, 0.1. The crystals, therefore, are disulphuret of copper and sesquisulphuret of iron, $Cu_2S + H_2S_3$.

The amorphous pyrites, however, is by no means a definite compound. It is an uncertain mixture of the sulphurets of

iron and copper, running into iron pyrites at one end of the scale and vitreous copper at the other. Generally pyritous ores grow richer as they are more deeply worked, the surface ores containing a larger proportion of iron than those which lie deeper. This may probably be accounted for on the same principle with the well-known phenomena of alloys. The heavier metal separates from the lighter, so that the sulphurets arrange themselves in the order of their specific gravity.

Copper pyrites is of a bright brass yellow color, opaque, with a conchoidal and uneven fracture, and a metallic lustre. It may be cut with a knife, those ores which are richest in copper yielding most readily. Its streak and powder are a rich blackish green or deep olive, shining with a dim yellow lustre. It tarnishes readily, and presents the most beautiful deep blue and iridescent tints.

Copper glance, or vitreous copper, is a fine lustrous deep gray ore, with a rich purple and greenish tarnish. It crystallizes in forms belonging to the right rhombic system. Klaproth's analysis of it is, copper, 78.5; sulphur, 19.6, with iron and silica. The last substances being accidental, the essential components, arranged in a percentage order, would be in the proportion of 80 to 20. The formula is Cu_2S.

This ore is one of the most commonly worked in the United States. Beautiful specimens of it are found at the Bristol Mine in Connecticut, the Central Mine, of New Jersey, and at Pipe Creek, in Maryland. In many of the States, it has been found in sufficient quantities to be worked to advantage.

The other copper ores, as malachite or native carbonate, dioptase, the oxides, the sulphate, the phosphate, atacamite, &c. do not constitute beds or working mines of themselves, but accompany the other ores. These rarer minerals, therefore, cannot occupy our attention.

METALLURGIC TREATMENT OF COPPER ORES.

The principal ores of copper which are smelted are the sulphurets, mixed, of course, with the silicates, carbonates, and other ores. The operations for this purpose are very various,

and too numerous and complicated for particular description in a work like this. The process adopted at Swansea, however, as described by Mr. Vivian, one of the largest smelters in Wales, gives such an insight into the behavior of copper during reduction, that it is worthy the attention of every student of chemistry.

The British ores are all poor. The average of the ore of Anglesey is only from 2 to 3 per cent., that of the Cornish copper about 8. The ore smelted in the United States, however, will generally average 20 per cent. of metal, the rich ore being sent to the furnaces in much larger quantity than the poor. Many of our American ores, when sent from the mines, are as rich as the metal obtained after the second smelting in Swansea. Ores from the Bristol and Central mines in Connecticut and New Jersey have frequently yielded from 48 to 51 per cent. by the dry assay. At one time, the smelters in Baltimore, then the chief smelting city in the Union, would purchase no ores that gave a lower average yield than 12 per cent.

The principles upon which the smelting of sulphuretted copper ores depends, will be clearly understood by a brief account of the common dry assay.

The ore to be assayed is reduced to fine powder, and introduced into a roasting dish, or a crucible which is laid obliquely in a furnace in such a manner that there may be a free circulation of air over the surface of the ore. The heat is at first very moderate, to avoid the agglomeration of the fine particles, and the ore is stirred briskly till it is uniformly heated through. The heat is gradually increased; blue flames of sulphur begin to play over the surface, and the ore becomes redhot. The stirring is kept up to bring every grain under the influence of atmospheric oxygen, and a glass rod dipped in solution of ammonia is occasionlly held over the crucible to ascertain whether acid fumes are still given off. When the rod moistened with ammonia no longer fumes when held over the crucible, the ore may be regarded as oxidated. All the sulphur, however, is not driven off. There remains a portion of it combined with the oxidated copper, as a sulphate. To get rid of this, finely pulverized carbonate of ammonia is to be added portionwise to the mass, and thoroughly incorporated by assiduous stirring. This

decomposes the sulphate of copper, and the volatile sulphate of ammonia is driven off in vapor. The ore is thus reduced to a mixture of oxides of copper and iron with gangue. It is now rubbed up with black flux, a little borax laid on top, and the whole fused till a clear, smooth, thin slag is formed. The copper will be found as a metallic button at the bottom of the crucible.

The object here is to get rid of the sulphur, and then, by fusion at a moderate heat in contact with carbon, to reduce the oxide of copper to a metallic state, at the same time that the alkalies of the flux and the earths and oxides of the ore form a fusible thin glass, which allows the heavy metallic globules of copper to fall through it in a shower and to collect at the bottom of the crucible.

The same end is attained, when working on the large scale, in a different manner. At many of the furnaces in Swansea, there are eight operations before the crude ore is reduced to refined copper. The first of these is the calcination of the ore, previous to which the ores are mixed in accordance with their respective richness and the varying nature of their gangue. The latter is essential, because the different earths contained in such a mixture mutually flux one another. The mixed ore is introduced into a calcining furnace, and gradually heated with constant stirring. Sulphur and arsenic burn off, the ore crumbles finer, the surface of the lumps are reduced to oxides, but the centres remain sulphurets. The ore is now transferred to a smelting furnace, in which it is ordinarily mixed with some crude or unroasted ore, with the richer portions of the slag from the same furnace, and with the scoriæ of more advanced smeltings. Here it is brought to a state of perfect fusion. The lighter oxides, the earthy matters, and the old slag combine in a glass of greater or less tenacity, while the metal, owing to its greater specific gravity, sinks down upon the sole of the furnace. Its accumulated slag is raked off from time to time, and fresh ore added till the coarse metal has reached the proper height. It is then drawn off into water, and coarsely granulated; more ore is added, the process going on continuously day and night. The scoriæ or slags are then broken up and picked over; those portions of them which contain globules of metal are sent back to the furnace. In Wales, these slags are worked down so

closely that they contain only the half of one per cent. of copper. In this country, however, the high price of fuel and labor will not allow such close working. One and a half per cent. of copper in slag will not pay for reduction.

The coarse metal obtained is a mixture of sulphurets of iron and copper. This is roasted precisely as the ore, but oxidation goes on with more rapidity, because the earthy matters which screened the sulphurets from the action of the air, have been removed.

The fourth operation is another fusion. To the calcined coarse metal, rich slags and cobbing* are added, and the smelting conducted as in the first fusion. The metal is either granulated or drawn off in pigs, according as it is to be calcined or not. The fifth process is a calcination of the produce of the second smelting. The sixth operation is the smelting of the last calcined metal. This is black or coarse copper; and it is transferred to a furnace, where it is first roasted and then smelted. The result of this operation is pig copper or blistered copper, as it is sometimes called. It is a mixture of metallic copper with oxide and a little sulphuret.

The eighth process is that of refining and toughening. This is a very nice and delicate operation, requiring great skill and experience on the part of the workman who undertakes it. The pig copper is laid on the sole of the refining furnace and allowed to remain at a low heat for several hours that a sort of roasting process may go on. The heat is gradually raised till the metal is melted. Its surface is then covered with charcoal to reduce the oxide combined with pure copper in the pig metal, the few scoriæ which have formed having been first raked off. The assay is now taken by dipping a small ladle into the metal and cutting and breaking the button, to see the condition of the copper. It is dark-red and coarse grained. A stick of green wood is then thrust into the metallic bath and briskly stirred round. The hydrogen and carbon thus obtained combine with the oxygen, and so reduce the metal to a pure state. If too much carbon be present, a brittle carbonate is formed, which must be reduced

* This term applies to old mortar and fragments of brick, &c., about the furnaces, which have become saturated with various compounds of copper.

by atmospheric air. The exact point is attained by frequent assays taken in the manner already described. When the copper is in the proper condition, it is malleable, of a fine red color, and its fractured surface has a beautiful silky or satin-like lustre. The refined metal is cast into ingots or granulated.

In operating upon rich ores, these processes are very much modified. There is no calcination requisite. Much sulphur is necessary, indeed, in order to prevent the slags from retaining too much copper, for the globules of sulphuret are larger and fall more readily through the fluid scoriæ, which are formed in the first smelting, and which, when the metal below them is too rich, contain innumerable small glittering specks of copper. This is independent of the fluidity of the slag, for I have seen slags as smooth as bottle-glass sparkling all over with these little specks. The ores are therefore directly fused, and the resulting *red metal*, as it is called, is smelted again with the richer slags. The white metal proceeding from this operation is again smelted with rich slag and brought to the condition of *regulus*, the minimum degree of sulphuration. The fourth operation is the reduction of this regulus to pig copper, which is subsequently refined in the manner already described.*

METALLURGIC TREATMENT OF THE ALLOYS OF COPPER.

To obtain pure copper from small quantities of alloy, recourse may be had to either the wet or the dry method. The latter process is called refining.

Refining on the small scale is exactly analogous to cupellation; indeed, it is a cupellation performed on copper. Some copper is wasted in the operation, being volatilized or carried into the cupel with the litharge. The operation is conducted in an ordinary cupelling furnace, but the temperature being necessarily high, it must have a strong draught. The phenomena are very much the same as those already described under the head

* There are many other processes which have been adopted, and modifications are constantly made in them; but it has not been thought necessary to introduce any account of them in this place.

of Silver. The same iridescent pellicle is formed; the same rotation of the button and the same sudden solidification are observed.

In the large way, an analogous reduction of alloys to copper has been successfully applied to bronzes and bell metals. Fourcroy invented the plan during the wars of the French Revolution. He oxidated the alloys thoroughly in a calcining furnace, and then fused a quantity of unroasted alloy with this mixture of the oxides. Metallic copper subsided, and scoriæ, composed of the oxides of tin and copper, floated on the surface of the bath. The scoriæ were then reduced, and the metal obtained from them treated in the same way as at first. When they were very rich in tin, the alloy obtained from them was skimmed during the oxidation, and thus reduced to the standard of bell metal, because the tin, oxidizing more readily than the copper, was found in greater quantity in the scoriæ. The metal, thus procured, was treated precisely in the same manner as at first.

The process of eliquation was also applied to the same purpose. The blocks of metal rich in tin were laid on the sloping hearth of a reverberatory furnace, and, by means of a regulated heat, the more fusible metal was gradually sweated out.

To obtain absolutely pure copper from the alloys of this metal by the humid process, the common method is to dissolve the alloy in nitro-hydrochloric acid, to evaporate to dryness with frequent moistening with hydrochloric acid, in order to drive off excess of nitric acid, and then to boil the solution with a strip of metallic zinc or iron till all the copper is precipitated, taking care to have the solution dilute and acidulous. When zinc is employed, the copper is pasty and adherent, and is very liable to oxidate when drying. Iron, however, usually throws down the metal in beautiful minute shining scales. Sometimes it precipitates the copper in thin sheets of considerable tenacity, smooth and shining on the side next to the iron, rough with little spangles on the other surface. However obtained, it is necessary to wash the precipitate well, first with dilute sulphuric or hydrochloric acid, and then with pure water. It must be dried in the water-bath. Too high a heat oxidates it.

Another method is to dissolve the alloy in the usual copper solvents, filter and treat the solution with ammonia. Potash, boiled with this solution, throws down the black oxide, which is to

be sharply dried, then introduced into a gun-barrel, or better, a porcelain tube, and heated to redness, while a stream of hydrogen gas passes over it.

COPPER AND ITS MORE SALINE COMPOUNDS.

Copper is distinguished from all metals, except titanium, by its color, which is a fine brownish red, slightly inclining to yellow. It is susceptible of a high but fugacious polish, as it is extremely liable to tarnish. It is soft enough to be cut with a knife, though more resistant than lead. Its malleability exceeds its ductility, so that, while it may be laminated in very thin leaves, it cannot be drawn out to extremely fine wire. In fine powder it welds like gold, a property which has been taken advantage of in the manufacture of medals. Fine copper powder is strongly forced into the die, and an unusually sharp and clear impression is thus obtained. The medal may be afterwards hardened by careful annealing. It has a faint, nauseous, disagreeable taste and odor.

The specific gravity of copper, fused in the open air (8.7 to 8.8), is lower than the average, because some oxygen is absorbed from the atmosphere and the metal rendered porous. Fused under a protecting slag, its sp. gr. is 8.91 to 8.921. That of the unignited wire is 8.939 to 8.949; of the ignited wire, 8.93; of flattened wire and sheet, 8.95. Its fusing point is 1,996°, intermediate between that of silver and of gold.

At a high temperature it is volatile, and even at its fusing point a considerable quantity of it escapes into the atmosphere. In the most carefully managed furnaces this loss is unavoidable, and usually amounts to the fourth of one per cent., or it may go much higher than this. In a properly conducted smelting establishment, the loss ought never to exceed the half of one per cent. All the ores of copper are volatile, and in a furnace without a culvert much metal must necessarily be lost. The author has known 20 tons of fine, impalpable, reddish dust, containing on an average 14 per cent. of copper, to be taken out of the culvert of a smelting establishment, as the residuum of about 3,000 tons of ore, averaging 22 per cent.

Its symbol is Cu; its equivalent, as determined from the re-

duction of the black oxide by hydrogen, is 31.71 on the hydrogen, and 396.7 on the oxygen scale. Some, who regard the black oxide as a deutoxide, make it 63.42.

Oxides.—When copper is fused in the atmosphere, tarnishes of various hues of yellow, red, purple, and black, form on its surface. These indicate various admixtures of the two oxides with metal, and may be conveniently seen on the surface of ingots sent to market. When these have been allowed to cool too long in the air after being cast, they are invariably coated with a black layer. When they have been immersed early in the water, the tarnish is either an orange yellow or a fine ruby red, or a mixture of these two. It is upon the proper management of this that the preparation of Japan copper depends. This is cast in small moulds, and the moment it has consolidated it is thrown into water, where it becomes covered with a beautiful red film of suboxide. Heated in oxygen or the flame of the compound blowpipe, copper burns with a rich green light, and is wholly converted into black oxide. Its tarnish, gradually acquired from the atmosphere, is at first a warm deep brown, which gradually passes into the dark olive-green, so highly prized by antiquaries, a color produced by the mixture of the carbonate and the two oxides. Acids corrode it and form salts with it which are poisonous.

Dioxide of Copper, Cu_2O. 71.42.—This compound occurs native, as red copper ore. It has been found amorphous, and in brilliant, blood red, half-transparent octahedral crystals. It is often found melted through quartz in the neighborhood of native copper, giving the silicious stone a beautiful ruby red color.

It may be made by calcining the metal in a muffle; or by igniting, in a covered crucible, a mixture of 31.71 parts of copper filings with 39.71 of black oxide, or 24 parts of anhydrous blue vitriol and 29 parts of finely divided copper. A very fine metallic pigment has been made by mixing intimately 100 parts of sulphate of copper with 59 parts of carbonate of soda; fusing these in their water of crystallization at a low temperature, and continuing the heat till the mixture is dry; then mixing intimately with them 25 parts of finely divided metallic copper, and heating the whole in a covered crucible to whiteness for twenty minutes. An analogous process of deoxidizing the black oxide

is heating to redness in a carefully closed crucible a series of alternate strata of fine copper sheets and black oxide of copper. The dichloride may be decomposed by carbonate of soda in a closed crucible, and the resulting chloride of sodium washed out, leaving the dichloride of copper. Or, lastly, a solution of one of the salts of the protoxide, say the acetate, may be boiled with sugar, when the red oxide of copper falls down. Trommer's test for saccharine urine depends on this reaction. This oxide is always formed when a large quantity of metallic copper is fused under scoriæ sufficiently thin to admit a little atmospheric air. It is often found on the sides of refining furnaces mixed with the black oxide, and then the mass is crystalline in its texture, dark gray in color, with metallic lustre, and flecked with magnificent ruby-red, semi-transparent patches.

This compound varies in color from a brownish copper red to a pure carmine tint. The hydrated suboxide is yellow. In a dry atmosphere it may be kept for a long time, but moisture rapidly peroxidates it. Heated to redness, it is converted into the black oxide. The acids act upon it variously. Most of them decompose it into a salt of the black oxide and metallic copper. Strong nitric acid oxidates it with the evolution of binoxide of nitrogen. Hydrochloric acid dissolves it, forming a colorless solution, from which the alkalies and their carbonates throw down yellow or red precipitates, and ferrocyanide and iodide of potassium white or brownish ones. Ammonia dissolves it to a colorless fluid, which rapidly becomes blue from absorption of oxygen.

Fused with glass, this oxide forms a fine rich ruby-red when proper care is taken to prevent oxidation. A little metallic tin is often mixed with it for this purpose. Its coloring power is very intense, so that an exceedingly thin film may be blown out as a coating to a vessel of transparent glass. The outer film may be then cut through, and various forms obtained in colorless glass. Pastes are also colored by it to imitate the ruby and the garnet.

Black Oxide of Copper, CuO. 39.71.—This oxide is also found native as copper-black, in amorphous earthy powder or lumps, and sometimes fused in the cupriferous trappean rocks. In the latter instance, it is commonly found investing the native copper,

and it always presents a brilliant metallic lustre. Its dark rich gray tint causes it often to be confounded with the vitreous ore of Brochant, or the Fahlerz of the Germans; from which, however, it may be easily distinguished by its solubility in hydrochloric acid without residue. The author has seen this oxide sublimed through the porous bricks of a refining furnace, and condensed in the cavities in bright, lead gray acicular crystals.

It is best prepared by igniting the crystallized nitrate in a platinum crucible, or by precipitating the blue ammoniacal solution by caustic potassa at a boiling temperature. Calcination of the metal gives a mixture of the oxides.

The color varies from a deep brown to a bluish-black. The hydrated oxide is blue with a slight cast of green. Its specific gravity is 6.401. At a high temperature, it fuses to the crystalline mass already described. Heated to redness with carbon or hydrogen, it is reduced to metallic copper. Deoxidating agents, such as protoxide of iron, protochloride of tin, and organic matters at a boiling temperature, convert it into dioxide. *Verditer* is a mixture of its hydrate and carbonate. Its solution in ammonia is blue.

The salts of this oxide are numerous. When anhydrous, they are commonly white; when hydrated, of a rich blue or green tint. From their solution, iron or zinc separates metallic copper, and the alkalies the greenish-blue hydrated oxide. Ammonia in small quantity throws down a pale bluish-green subsalt, and in excess dissolves it again, forming an ultramarine blue solution. The carbonates throw down a greenish-blue precipitate, which is a mixture of carbonate and hydrated oxide. It is precipitated white by iodide of potassium; mahogany brown by ferrocyanide of potassium; dark brown or black by sulphuretted hydrogen; brownish-yellow by ferridcyanide of potassium; reddish-brown by chromate of potassa; white, with a shade of beryl green, by oxalic acid. A clean rod of iron is stained with a solution of copper, containing 1 part of the oxide in 100,000. Tincture of guaiacum gives a blue tint, changing to green with a solution containing 1 part of copper salt to 450,000 of water. Ferrocyanide of potassium will give a mahogany tint to 651 gallons of water, holding in solution a grain of copper. Albumen throws down an insoluble yellowish-white precipitate, which has been proved

by Orfila to be inert; so that albumen may be used as an antidote to poisoning by copper.

Peroxide of Copper, CuO_2. 47.71.—Thenard obtained this compound by acting on the hydrated oxide with peroxide of hydrogen. It undergoes spontaneous decomposition under water, but may be dried over sulphuric acid *in vacuo*.

Cupric Acid.—When nitrate of copper is added to a solution of bleaching salt, with excess of lime, at a temperature below 32° F., the bluish-green precipitate becomes purplish-red. It is washed with cold lime-water. Its formula seems to be Cu_2O_3.

Sulphurets.—There are several combinations of copper and sulphur.

Disulphuret of Copper, Cu_2S. 79.52.—Occurs native as *copper glance*. It may be formed artificially by heating copper filings with finely divided sulphur, and by acting on copper foil by vapor of sulphur.

This is a very fusible and somewhat volatile compound. Ignited in atmospheric air or oxygen gas, it is converted into the black oxide, sulphurous acid, and sulphate of copper. Fusion with saltpetre produces oxide of copper and sulphate of potash; with the alkaline carbonates and charcoal, a small quantity of metal and a large bead of regulus. Ignition with oxide of copper expels sulphurous acid, and leaves metal or suboxide.

Sulphuret of Copper, CuS. 47.81.—This compound is found native as *copper indigo*. It is precipitated when a salt of copper is treated with sulphuretted hydrogen. Thus obtained, it is brownish-black, easily oxidated, converted into a sulphate by exposure to the air, by roasting, or by fusion with nitre.

There are several other sulphurets of copper, of which the proto-sulphuret is unchangeable in the air and soluble in alkaline carbonates. An oxysulphuret, according to Pelouze, of the former, $5CuS + CuO$, is produced when a sulphuret in solution is poured into a copper salt.

Phosphurets.—*Phosphuret of copper*, obtained by igniting copper with phosphorus, or phosphate of copper with charcoal, is a mixture of copper of different degrees of phosphorization, fusible, nearly as hard as steel, brittle, of a color varying from copper red to steel gray, in proportion to the percentage of

phosphorus. When phosphuretted hydrogen is passed over phosphate of copper, Cu_2P is obtained. A *subsulphophosphite* is formed when bisulphuret of copper is treated with sulphuret of phosphorus, and gently warmed in a current of hydrogen. It is a yellow powder, of the composition $2CuS,PS_3$. By heating this, two equivalents of sulphur are driven off, leaving $2Cu_2S,PS$.

The *hyposulphophosphite* (CuS,PS) is obtained like the last compound by using the sulphuret of copper instead of the bisulphuret. Various salts are formed from it by decomposing it through the agency of heat.

Nitruret of Copper.—Nascent copper at a high temperature has an affinity for nitrogen, and forms a definite compound with it, Cu_6N. It is a greenish powder, obtained by passing perfectly dry ammoniacal gas over oxide of copper heated in a glass tube to 482°. Nitrogen and water are also produced, and the decomposition is attended by a remarkable rise of temperature. At a heat of 572°, the compound is resolved into nitrogen and metallic copper.

Hydruret of Copper.—When from a solution of 10 parts hypophosphite of baryta all the baryta is exactly precipitated by the addition of sulphuric acid, and 8 parts of sulphate of copper are then introduced into it, a heat of 158° will throw down a precipitate, first yellow and then orange. Should bubbles of hydrogen escape, the vessel must be cooled. The deposit is to be collected on a filter and washed in an atmosphere of carbonic acid, with water deprived of air. It is then to be dried between folds of bibulous paper. Its composition is supposed to be Cu_2H.

ALLOYS OF COPPER.

Copper unites with most of the metals, forming many alloys of the greatest practical value. The most ancient of these are the compounds of copper and tin. Antique swords were made of these two metals in varying proportions. A sword found in the peat moss of the Somme contained copper, 87.47; tin, 12.53. Another, found near Abbeville, was composed of 85 copper to

15 of tin, and another, of 90 of copper to 10 of tin. The bronze springs of the balistæ were made of copper 97, tin 3.

The application of bronze to the casting of statues had its origin in a very remote period. It was not, however, brought to anything like perfection till about 700 years before the Christian era, after which time it became a favorite material for statues. To this purpose it is well adapted, as it expands in cooling, and is thus forced up into all the little inequalities of the mould, giving a clear sharp outline not to be obtained from any other material. It requires, however, much skill to manage it properly. Besides the property of alloys, already alluded to, to separate into strata, according to the specific gravities of the metals composing them, the varying affinities for oxygen of the component parts of bronze, is another difficulty in the way of the artisan. The column of the Place Vendome, in Paris, is an example of the inability of the artist to overcome this obstacle. The bass-reliefs of the pedestal of this column contain 94 per cent. of copper, those of the shaft much more, and those of the capital 99.79. The founder, therefore, had gone on driving off his tin by oxidation till there was scarcely any of it left. The cannon from which these castings were made contained 89.36 per cent. of copper, and 10.04 of tin, the rest being made of other metals. The ancient bronzes are composed of copper and tin alone. Many of the modern are brass with excess of copper, or a mixture of brass, lead, and tin. Bronze for medals is composed of from 8 to 12 parts of tin, and 92 to 88 of copper. Two or three parts of zinc give it a finer bronze tint.

Bell metal, of the finest quality, should be composed of copper 78, tin 22, but the founders increase their profits at the expense of the sonorous properties of the alloy, by adding zinc and lead to the mixture. Chinese gongs have the above-named composition, varying to 81 of copper and 19 of tin. They contain no other metal.

Cannon metal is composed of copper 90 or 91 and tin 10 or 9.

Speculum metal, very white and brilliant, is composed of copper $66\frac{1}{3}$, tin $33\frac{1}{3}$. Brass and arsenic are often added to this.

Copper and Arsenic form a white alloy, sometimes used for

thermometer and barometer scales, dials, &c. It is composed of 9 parts of copper to 1 of arsenic. To attain this proportion, however, it is necessary to introduce $3\frac{1}{2}$ parts of the latter metal before fusion, which operation is conducted under salt, in a closed crucible.

German silver is composed of copper, 40.4; nickel, 31.6; zinc, 25.4; iron, 2.6. This is the genuine German silver, but there are many imitations and modifications of it made after a great variety of formulæ.

Brass is a compound of copper and zinc, in varying proportions. During the melting of the two metals together, a considerable loss of the zinc takes place in consequence of its ready volatility and combustibility, so that more zinc must be added than the alloy is desired to retain. The exact determination of the extent of this volatilization is a matter of some nicety, and, as it depends on a variety of circumstances, such as the temperature and draught of the furnaces, the mode of admixture of the two metals, &c., the manufacture of good brass requires not a little skill and experience on the part of the workman. Common brass is a very irregular and carelessly made compound, much contaminated with tin and lead arising from the solder. Yellow metal, or sheathing brass, is usually rated at 60 copper and 40 zinc, the object of the manufacturer being to introduce as much as possible of the cheaper metal without injuring the malleability of the compound. Practically, however, its composition is variable, though, in good sheathing metal, it always approximates these proportions.

The finest brass consists of about 63 of copper to 32 of zinc ($ZnCu_2$), to which about 2 parts of lead are added when the brass is to be turned. Brass for hammering consists of 70 of copper to 30 of zinc. Mannheim gold consists of 75 copper and 25 zinc, separately melted and suddenly incorporated by stirring. Prince's metal, Dutch foil, similor, and pinchbeck are of similar composition. Red brass, called tombac by some, is brass with excess of copper, the proportions varying from $2\frac{1}{2}$ to 8 or 10 of copper to 1 of zinc. Mosaic gold, *aurum musivum*, according to Parker and Hamilton's patent, consists of 100 of copper to 52 or 55 of zinc. *Brass solder* is composed of equal

weights of the two metals, or two parts of brass and one of zinc melted together, to which a little tin is sometimes added. Copper is sometimes roasted with brass by exposing it to the vapor of zinc. The spurious gold wire of Lyons is made in this manner. Copper vessels are coated with brass by boiling them in a solution of argol and zinc amalgam in hydrochloric acid.

Brass melts at 1869° Fahrenheit, and loses a considerable proportion of zinc. At white heat it still retains 16 per cent. of this metal, and, even after a protracted fusion at this high temperature, 3 or 4 per cent. of zinc remains. Zinc can be driven off entirely by a carefully conducted calcination in the open air.

Besides the numerous uses to which metallic brass is applied, it is also employed by the workers in colored glass to stain their wares. For this purpose it is repeatedly calcined till a brown powder is obtained, which makes the glass intumesce when fused with it. It communicates various tints of green, passing into turquoise. A chalcedony red or yellowish tinge is obtained from a vitrifiable pigment, made by stratifying brass and sulphur in a crucible, calcining them at a red heat, and then roasting the resulting powder in a reverberatory furnace.

Copper forms alloys with molybdenum, tungsten, manganese, and iron. As a general thing, copper, alloyed with iron or lead, flattens out evenly to a certain thinness, and then breaks around the edges. The author, however, has succeeded in obtaining a malleable alloy of copper and iron which had a perfect coppery appearance and lustre, by fusing an intimate mixture of the two oxides with black flux in the full heat of an air furnace. The button obtained from this experiment had all the appearance of fine copper, laminated under the hammer to a very thin sheet with perfectly unbroken edges, and yielded, on analysis, 33 per cent. of iron. Arsenic, antimony, and bismuth form brittle alloys with copper.

HALOID SALTS.

Chlorides. *Subchloride of Copper*, Cu,Cl. 98.89.—When corrosive sublimate is heated with half its weight of copper filings, mercury passes over, and dichloride of copper remains

behind. Boyle, who procured it in this way, called it *resin of copper*, from its resemblance to common resin. Proust called it *white muriate of copper*, and obtained it by the action of protochloride of tin on protochloride of copper. Ignition of the chloride with sugar in a closed crucible also produces the subchloride. It is slowly deposited in crystalline grains when protochloride of copper is kept in contact with metallic copper. It is deposited on a plate of copper suspended in a solution of the chloride, in the form of white tetrahedral crystals.

The dichloride is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. Its color varies with the mode of preparation, being white, yellow, or dark brown. It is apt to absorb oxygen from the atmosphere, forming a green compound of oxide and chloride of copper. It is insoluble in water or dilute sulphuric acid, but dissolves in hydrochloric acid, and is precipitated as a white powder by water. It is also soluble in water of ammonia and in a solution of common salt.

Chloride of Copper, CuCl. 62.18.—Sometimes this salt is prepared by double decomposition, by mixing sulphate of copper and chloride of sodium together, and crystallizing the sulphate of soda and excess of salt out of the solution. It is much better obtained by dissolving oxide or carbonate of copper in hydrochloric acid, or the metal in nitro-hydrochloric acid.

Duly evaporated, the solution thus obtained yields four-sided prisms (CuCl+2HO), of a rich emerald green color, deliquescent and soluble in alcohol. At 212° they lose water, and when treated with cold sulphuric acid all their water is separated, and brown anhydrous chloride is left. This is fusible, and may be sublimed unchanged.

Basic Chloride of Copper, Cu,Cl,3CuO+4HO, *Brunswick Green.*—This is a well-known pigment, formed by digesting hydrated oxide of copper in a solution of the chloride, or more commonly by exposing copper plates, moistened with sal-ammoniac, to the action of the atmosphere. It is a green powder, soluble in acids, not in water. On the application of heat, it loses water and becomes brownish-black.

When chloride of copper is precipitated by a small quantity

of potassa, a pale green powder is thrown down, having the composition $CuCl,2CuO+4HO$. Heated strongly, it becomes black, all the water being driven off, the formula then being $CuCl,2CuO$. Kept at 208°, a brown compound is left, $CuCl,2CuO+HO$. The black substance, moistened, becomes $CuCl,2CuO+3HO$.

Chloride of Copper and Ammonium, $CuCl,NH_4Cl+2HO$.—This salt is obtained by mixing saturated solutions of chloride of ammonium and chloride of copper. It crystallizes in beautiful blue rhombs, soluble in water. When warm chloride of copper is saturated with ammoniacal gas, ammonio-chloride of copper, $CuCl,NH_3$, is formed, which is decomposable by water. This dissolves a biammonio-chloride, $Cu,Cl,2NH_3$. This is blue and crystallizable. A triammonio-chloride, $CuCl,3NH_3$, also exists.

A double chloride of copper and potassium is formed by cooling a strong mixed solution of the chlorides of the two metals. It crystallizes in octahedra, belonging to the quadratic system, of the form $KCl,CuCl+2HO$. The subchloride used instead of the chloride furnishes a double salt, $2KCl,Cu_2Cl$, crystallizing in anhydrous octahedra of the regular system.

Bromide of Copper, CuBr. 115.1.—Oxide of copper dissolved in hydrobromic acid and evaporated, forms green crystals of the form $CuBr+5HO$, which, by heat, separate into bromide and subbromide, Cu_2Br. Dry bromide absorbs ammonia, becoming $CuBr,5NH_3$. There are several other ammonio-bromides, and a basic salt, none of them of any particular interest.

Diniodide of Copper, Cu_2I. 172.71.—When a solution of iodide of potassium is added to another of blue vitriol, one-half the iodine escapes, sulphate of copper remains in solution, and a brownish-white subiodide of copper with finely divided iodine falls. The latter is washed off with alcohol. The subiodide is fusible and easily decomposed by nitric and sulphuric acids and by alkali. The iodide has not been separated. A blue ammonio-iodide, however, exists, having the form $CuI,2NH_3+HO$.

Subfluoride of Copper, Cu_2F. 82.18.—Hydrofluoric acid brought in contact with hydrated suboxide of copper converts it into a

fusible subfluoride. The silico-subfluoride, $3Cu_2F,2SiF_3$, resembles it in color and character.

Fluoride of Copper, CuF_3. 92.93.—Fluoric acid forms with black oxide of copper a blue solution, from which the terfluoride separates in crystals containing 2 equivalents of water. It forms green, soluble, double salts, with the alkalies and alumina. A basic fluoride ($CuF,CuO+HO$) is formed by treating the blue fluoride with hot water.

A *borofluoride* is obtained by decomposing sulphate of copper with borofluoride of barium. It separates in blue, deliquescent, crystalline needles, of the form CuF,BF_3. The *silico-fluoride* is in blue prisms, containing 21 parts of water, 2 of which are separated by the effervescence of the salt.

OXYSALTS.

SALTS OF THE SUBOXIDE.

Sulphite of Suboxide of Copper.—When sulphurous acid is poured upon hydrated oxide or carbonate of copper, a double decomposition ensues; thus $3CuO+2SO_2=CuO,SO_3+Cu_2O,SO_2$. Sulphate of copper is formed at the expense of one part of the oxide and is dissolved, and the remaining dioxide unites with the sulphurous acid, forming a sulphite of the suboxide. It may be obtained in crystals by warming a filtered mixture of the solutions of sulphate of copper and caustic potassa, neutralized with sulphurous acid.

It is a brilliant red salt, unchangeable when dry, soluble in hydrochloric and sulphuric acids and in ammonia; insoluble in water. Sulphuric acid and heat decompose it.

Hyposulphite of Suboxide of Copper, obtained by treating the sulphate with hyposulphite of lime, is a colorless solution. It forms several double salts with potassa and soda.

Silicate of Suboxide of Copper.—This is the substance already described as the coloring matter of red glass. It is found native in the quartz which surrounds native copper.

SALTS OF BLACK OXIDE.

Sulphate of Copper, CuO,SO_3. 76.81.—This salt is a common product of mines of sulphuret of copper. The ore is oxidized by the joint action of air and moisture, and the water which trickles over it washes off the newly-formed sulphate. This natural process has been imitated by manufacturers who calcine the native or artificial sulphuret, lixiviate it and crystallize. Addition of sulphuric acid increases the product. It is also obtained by dissolving the metal in moderately dilute sulphuric acid and crystallizing.

As prepared by the first two processes, it is always impure, containing sulphate of iron. This may be in great measure separated from it by calcination, which decomposes the sulphate of iron, leaving the oxide, but does not affect the blue vitriol. The copper may also be precipitated by means of iron and redissolved in sulphuric acid.

Pure sulphate of copper is a clear azure blue salt, crystallizing in elongated rhombs of the doubly oblique rhombic or triclinate system. These contain 32 parts of oxide of copper, 32 of sulphuric acid, and 36 of water in the hundred parts, and may be expressed by the formula CuO,SO_3+5HO. A small quantity of iron is recognized by the greenish cast it gives to the crystals, and especially to their effloresced surfaces. The specific gravity of the salt is 2.274. Exposed to the atmosphere, it parts with a quantity of its water and effloresces; at 212° it loses 4 equivalents of water; at 430°, it parts with the remaining atom, leaving the anhydrous sulphate as a white, opaque, pulverulent mass. The anhydrous salt is obtained in colorless crystals by the action of cold sulphuric acid on copper in close vessels. However obtained, it attracts water from the atmosphere. Strong ignition expels its acid, and, if carbon be present, sulphuret of copper and metallic copper remain at a high temperature, and metal alone at a low one.

Basic Sulphate of Copper.—A compound of this sort forms the basis of the mineral *Brochantite*. It is prepared artificially by precipitating the sulphate already described with a small

quantity of alkali, by digesting fresh carbonate or hydrate of copper in a solution of blue vitriol, or by exposing ammonio-sulphate to the action of the air. It is pale green, insoluble, easily decomposed by heat into water, oxide and sulphate of copper. It is supposed to be a mixture of two basic salts, and the expression for it will be found between the formulæ $4CuO, SO_3+4HO$ and $3CuO,SO_3+3HO$. Kane says that, by exactly precipitating blue vitriol with caustic potassa, he obtained another basic salt, the composition of which is $8CuO,SO_3+12HO$.

Sulphate of Copper and Ammonia.—There are several double salts of copper formed with ammonia and potassa. The ammoniacal double salts vary much in color and composition. When solutions of the two sulphates of copper and ammonia are mixed, and duly concentrated, we obtain light blue, very soluble crystals, of the form NH_4O,SO_3+CuO,SO_3+6HO. When carbonate of ammonia and sulphate of copper are rubbed together in a mortar, the mass becomes blue, effloresces and grows moist, and another double salt is formed. When a strong solution of blue vitriol is treated with water of ammonia till the insoluble sub-salt first thrown down is all dissolved, we obtain an ultramarine blue solution, from which, by gradual evaporation, cold, or the addition of alcohol, blue prisms of ammonio-sulphate of copper separate. Their formula is $2NH_3+CuO,SO_3+HO$. They are soluble in $2\frac{1}{2}$ parts of water, and decompose in the air. At 300° they become apple green, having parted with their water and one equivalent of ammonia, and at 400° one-half of this is dispelled. Dry sulphate of copper absorbs 53.97 per cent. of ammoniacal gas, forming a soluble blue powder, $5NH_3+2(CuO,SO_3)$.

Sulphate of Copper and Potassa is a light blue salt, formed by crystallizing the mixed solution of the sulphates. It is KO,SO_3+CuO,SO_3+6HO. It loses two equivalents of water at 212°, and deposits a green basic double salt on boiling. The double sulphate with soda is formed in the same manner from blue vitriol and bisulphate of soda. A salt composed of the sulphates of copper, soda, and magnesia, may be formed by mixture and crystallization.

Hyposulphate of Copper, CuO,S_2O_5+4HO.—When sulphate of copper is exactly decomposed by hyposulphate of baryta,

and the solution concentrated, rhombic prisms soluble in water are obtained, from which a small quantity of ammonia precipitates a basic hyposulphate, and with which an excess of the same reagent forms a double salt which crystallizes in azure square tables, difficult of solution, permanent in the air, and composed of $2NH_3 + CuO,S_2O_5$.

Phosphate of Copper, $2CuO,PO_5$. 111.11.—Phosphate of soda throws down from a soluble salt of copper, the above salt as a greenish powder, insoluble in water, soluble in acids, becoming brown by heat. A number of basic phosphates have been found native. The *phosphite* and the *hypophosphite* of copper possess no particular interest.

Nitrate of Copper.—When nitric acid is poured upon metallic copper, violent action takes place even in the cold. Strong effervescence ensues; heat is evolved; copious, dense, red fumes rise, and a blue solution is obtained. The reaction will be understood by a glance at the formula. Thus $3Cu + 4NO_5 = 3(CuO,NO_5) + NO_2$. The deutoxide of nitrogen as it rises absorbs oxygen, and forms the red fumes of nitrous acid. To obtain the solution, concentrated nitric acid must not be used, as a green basic insoluble salt will subside. The crystals, obtained from this solution at low temperatures, contain 6 equivalents of water; those procured at high temperatures only $3(CuO,NO_5 + 3HO)$. The crystals, which are fine blue prisms, are highly deliquescent, and it is almost impossible to keep them. They deflagrate on redhot coals, and behave generally like other nitrates. Powdered and rolled in tin-foil, they are spontaneously ignited. The basic salt, $3CuO,NO_5 + HO$, is formed by heating the neutral salt in solution with a little alkali. It is a green powder, soluble in acids, not in water, easily reduced by a red heat to a black oxide, as is the crystallized nitrate. Treated with ammonia, it forms the ammonio-nitrate, the formula of which is $2NH_3 + CuO,NO_5$.

Carbonate of Copper.—This compound occurs native in the beautiful green and blue malachites. It is obtained artificially by precipitating it from a hot solution of copper with an alkaline carbonate. When precipitated from a cold solution, it is mixed

with the hydrate, and contains a large quantity of water. Ure's formulæ for this salt are :—

$$2(CuO,CO_2)+CuO,HO.$$
$$CuO,CO_2+2(CuO\ HO).$$

Borate of Copper is a pale green powder, slightly soluble in water, fusing to a green glass. It may be obtained by fusing borate of soda and oxide of copper together and dissolving out the soda, or by double decomposition.

Silicate of Copper occurs native as a fine apple green compound, usually in botryoidal shapes. It is formed by fusing oxide of copper with glass, and has a green tint.

Acetates of Copper.—There is quite a number of these salts. The neutral acetate, obtained by dissolving verdigris in acetic acid, or by precipitating an equivalent of sulphate of copper with an equivalent of neutral acetate of lead, crystallizes in dark green, oblique rhombic prisms, with oblique terminating planes. *Verdigris* has been called a bibasic acetate of copper, but analyses of it do not very closely correspond with its theoretical composition. It is a green salt, largely used in the arts. It is formed by the action of vinegar upon plates or sheets of copper.

Arsenites of Copper. Scheele's Green.—This fine pigment is formed by precipitating sulphate of copper with arsenite of potassa. The *Schweinfurth green*, which is a richer pigment, is made by boiling strong solutions of acetate of copper and arsenious acid together. It is a mixture of arsenite and acetate of copper. There is another arsenite of copper ($2CuO,AsO_3$), which is precipitated neither by acids nor alkalies, and which furnishes a yellowish-green salt by evaporation. It is made by digesting the oxide or the carbonate of copper in arsenious acid.

CHAPTER V.

ZINC.

This metal was first mentioned by Paracelsus, under the name of zinctum, in the 16th century. Its most abundant ore is the sulphate or blende, but *calamine*, a mixture of silicate and carbonate, is more easily worked. It is known in commerce by the name of spelter.

METALLURGIC TREATMENT OF ZINC ORES.

When sulphuret of zinc is to be smelted, it is always roasted so as to drive off the sulphur and convert it into an oxide. This is commonly done in a reverberatory furnace. It is then variously treated in the different countries in which it is smelted.

In Silesia, the roasted ore is mixed with its own volume of coal-cinder and introduced into redhot muffles. These muffles are furnished with a conical neck and two openings, through one of which the zinc is drawn off, and through the other a fresh charge of ore is introduced. A single square furnace contains 10 muffles, 5 on a side, heated by a single fire. Every ton of metal requires from 11 to 12 tons of coal for its reduction, and 33 muffles are destroyed for every 50 tons of metal. The annual production of Silesia is from 7000 to 8000 tons of zinc.

At Liege, earthen tubes, about 3 feet long and 4 or 5 inches wide, holding about 40 pounds, are used for the reduction. They rest on fire-brick only at either end, the rest of the tube being exposed to the fire. They terminate at one end in cast-iron tubes, which contract in diameter from one to one and a half inch. Each furnace contains 22 such tubes laid horizontally in rows. The heat from a single fire plays freely over them. Into the earthen tubes the roasted ore, mixed with from one-half to two-thirds of its weight

of fine coke, is introduced. Heat is applied, and the condensed metal is drawn off, every two hours, from the cast-iron tubes.

The English use covered crucibles, with openings in the bottom, communicating with short conical tubes of sheet-iron, to each of which, during the process of smelting, a long sheet-iron tube is attached. These are heated in a circular cupola furnace, resembling a glass furnace, set in a high conical chimney with a strong draught. The cupola has several openings in it, through which the smoke and flame pass. The fire is made in the centre, and heats all the pots. The mixed ore and coal are placed in these pots, the hole in the bottom of which is closed with a plug, and heated. At first a *brown flame*, containing cadmium and arsenic, arises, then a bluish-white blaze plays over the surface. This is the signal for putting the covers on the crucibles, as it shows that the volatilization of the zinc has begun. The plug is now charred, and the vapors of zinc descend through the sheet-iron tubes and are condensed in a vessel of water, in which they terminate. When the tubes become choked, they are cleaned out with a redhot iron rod. The consumption of coal is about 12 tons to every 1 of metal. The granulated zinc is submitted to a second distillation.

The theory of these processes is simple. The roasting drives off sulphur, and the resulting oxide, mixed with coal and heated, is reduced, carbonic acid being given off. The volatile metal, passing off, is first liquefied and then solidified.

ZINC AND NON-SALINE COMPOUNDS.

Zinc.—The commercial metal is never pure. The best varieties are the Vieille Montagne and New Jersey zinc. The most of the zinc in the market is extremely impure, containing iron, lead, cadmium, arsenic, carbon, &c. It is impossible to get rid of these in the dry way by any process yet invented.

The only method is to dissolve the metal. If sulphuric acid be selected as the solvent, it will at once rid us of the lead, especially if some alcohol be added to the moderately dilute solution, as this metal then falls to the bottom as an insoluble sulphate. If a stream of sulphuretted hydrogen be passed through

the acid solution, the cadmium and arsenic are precipitated. The iron is now thrown down by carbonate of ammonia, which is added in sufficient quantity to redissolve whatever zinc may have fallen. The filtered solution is now evaporated to dryness, ignited, mixed with finely levigated charcoal, and distilled. A second distillation removes what carbon it may retain from the reduction.

It is a bluish-white, brilliant, crystalline metal, with large laminæ. It may be obtained in six-sided prisms. It is so hard that the file does not readily act on it. At ordinary temperatures it is somewhat brittle, and at 400° so much so as to be pulverizable in a mortar. At 200° or 300°, however, it may be rolled into sheets or drawn into wire. It remains unaltered in dry air, but in moist air it becomes dull. It does not decompose pure water, but when ignited it resolves steam into its elements. Acidulated water is rapidly decomposed by it, alkaline slowly.

The specific gravity of pure fused zinc is 6.9; of the common rolled metal, 7.19. It fuses at 773°; volatilizes at a white heat, and burns in the air.

This metal shrinks but little as it cools, so that it retains upon its surface any interstices or irregularities of the mould in which it is cast. On this account, as well as by reason of its cheapness, it has been used by dentists to take copies of their plaster-moulds of the mouth, for the purposes of plate-work. Bronze is an alloy which possesses the property of expanding during cooling in a very high degree, accurately representing, when well fused, the most minute peculiarities of the matrix, and would, consequently, do better work. Its price, and the difficulties to be encountered in its management, will probably prove an obstacle to its general adoption. The beautiful statuettes of *Berlin iron*, as the material is called, so much admired for their sharpness of outline, are often made of zinc, but the fine effect of their surface is manifestly obtained by careful chasing. Zinc may be made much more sensitive to the inequalities of the mould by mixing it with tin, and a combination of this kind is used instead of pure zinc by many dentists. Zinc, alloyed with copper, on the other hand, or lead, has a tendency to contract, and consequently to withdraw its surface from the inequalities of the mould.

Its symbol is Zn. Its equivalent is 32.527 on the hydrogen, and 406.59 on the oxygen scale.

Oxide of Zinc, ZnO. 40.54.—When metallic zinc is heated in an open crucible, it burns with great rapidity, sending up a bright bluish-white blaze, which lets fall a very light, downy, flocculent substance, formerly called *lana philosophica*, or philosopher's wool, and more recently flowers of zinc. It is the oxide. The same substance may be obtained by igniting the precipitated carbonate of zinc, and, in the form of a hydrate, by precipitating a solution of zinc by less potassa than is necessary to throw it all down.

When hot, it is straw or lemon yellow, but, if it be pure, it becomes white again on cooling. It is insoluble in water, but, being a strong salifiable base, it unites readily with acids. It also forms compounds with some of the alkalies.

The salts of this oxide are colorless, generally soluble in water, communicating to it a disagreeable styptic taste. The caustic alkalies throw down a white precipitate, soluble in excess. The carbonates produce a white precipitate, carbonate of ammonia being the only one which redissolves it when added in excess. The oxide being soluble in salts of ammonia generally, these prevent its precipitation. Sulphuretted hydrogen throws down all the zinc as a sulphuret from its solution in a feeble acid or from an alkaline solution. Alkaline sulphurets precipitate from any solution.

The gray film formed on zinc exposed to the air has been called a *suboxide*, but appears to be a mixture of the oxide and metallic zinc. Thenard speaks of a *peroxide* obtained by the action of peroxide of hydrogen on the hydrated oxide. The native crystallized oxide is red.

Sulphuret of Zinc, ZnS. 48.66.—This compound is found native in *blende*. When obtained by igniting the dry oxide or sulphate with sulphur, or the latter with charcoal, it is yellowish or white. The hydrate procured by precipitating the solution of the oxide by an alkaline sulphuret is white. Both are fusible at a high heat, and oxidized by roasting or by the strong acids. Hydrogen passed over ignited sulphate of zinc, leaves a yellow powder, ZnO,ZnS.

Phosphuret of zinc is a lead-colored metallic mass, formed by throwing phosphorus in melted zinc. It is slightly malleable. Carburet exists in commercial metallic zinc.

ALLOYS.

The most important alloys of zinc have already been mentioned under the head of Copper. It alloys readily with potassium and sodium, not easily with arsenic and antimony, and not at all with bismuth. In small quantity it unites with iron, which, when coated with it, goes by the name of *galvanized iron*. It protects iron, but is itself more subject to corrosion. It has been shown that when it contains the latter metal, it dissolves in acids far more readily than when pure, and that, under caustic potassa in contact with iron, it dissolves twelve times more rapidly than when in the same relation to platinum. Alloyed with tin, it forms spurious silver leaf.

HALOID SALTS.

Chloride of Zinc, ZnCl. 67.96.—This compound is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas. It is also obtained by dissolving the metal in hydrochloric acid, and distilling over the volatile chloride, the remainder being oxychloride, or heating it in a tube through which dry hydrochloric acid gas is passed. One part of zinc filings distilled with two of chloride of mercury, or one part sulphate of zinc with two of common salt, produce the same substance.

Thus obtained, it is a soft white solid at ordinary temperatures, and hence called *butter of zinc*. It fuses at a heat a little above 212°, sublimes at a red heat, and deliquesces in the air. It is soluble in alcohol, and crystallizes out of the solution in combination with the solvent. From a highly concentrated aqueous solution it may be obtained in crystals of $ZnCl+HO$.

There are several basic chlorides. When zinc is boiled with its chloride as long as hydrogen comes over, or when the chloride is incompletely precipitated by ammonia, a white powder results, which is $ZnCl+3ZnO+4HO$.

This chloride forms double salts with the alkaline chlorides. The double salt with ammonium is used for tinning iron or copper. When rubbed on the heated surface of the metal, the oxides present form double chlorides with the zinc salt, and ammonia is set at liberty, leaving a clean surface for the coating metal.

Iodide of Zinc, ZnS.—Iodine and water, digested on zinc filings, give rise to a colorless solution, which is evaporated to a deliquescent iodide. By heat, in close vessels, it sublimes in brilliant acicular crystals. Heated in the air, it decomposes into protoxide of zinc and iodine.

There are several basic and double iodides. Iodide of potassium and nitrate of zinc mixed together form a peculiar, soluble, crystallizable double salt, insoluble in alcohol, consisting of iodide of zinc and nitrate of potassa.

Bromide of Zinc, ZnBr.—This salt is obtained by dissolving the oxide in hydrobromic acid. It dissolves in water, alcohol, and ether, crystallizes with difficulty, fuses at a red heat, and in close vessels sublimes in needles. Heated in the air, it forms oxybromide. Ammonia unites with it to form a crystallizable salt.

Fluoride of Zinc, ZnF.—This salt is made like the bromide. It crystallizes, dissolves with difficulty in pure water, easily in water acidulated with hydrofluoric acid. There are several double salts, with potassium, aluminum, &c., and with the metalloids.

OXYSALTS.

Sulphate of Zinc, ZnO,SO_3.—This salt may be made by calcining the sulphuret, or by dissolving the metal or its carbonate in sulphuric acid. The same precautions must be observed, in order to insure purity, as have been already described under the head of metallic zinc.

It is isomorphous with Epsom salts, and, like it, crystallizes in different forms and with different proportions of water. Crystallized from a cold solution, it contains 7 equivalents of water, from a hot one, 6. By treating the former with alcohol, or

adding excess of acid to the crystallizing solution, the salt retains only 2 equivalents of water. When boiled with alcohol of 860°, the salt has 5HO. At 32°, 100 parts of water dissolve 43.02 of the anhydrous salt, and at 212°, 95.03. It is insoluble in alcohol stronger than .88. The dry salt is decomposed only at a very high and long continued heat. It forms a great variety of basic and ammoniacal salts.

Sulphite of Zinc.—This salt crystallizes from a solution of the oxide in sulphurous acid. It is soluble in sulphurous acid, precipitated by alcohol. Its formula is ZnO,SO_2+2HO.

Dithionate of Zinc, ZnO,S_2O_5+6HO, is formed by mixing sulphate of zinc and dithionate of baryta. It is very soluble, difficult of crystallization, and forms a double salt with ammonia.

Dithionite of Zinc is formed when the metal is digested in liquid sulphurous acid. Sulphite and hyposulphite are formed, for $ZnO+3SO_2=ZnO,S_2O_2+ZnO,SO_2$. The sulphite may be precipitated by alcohol, or converted into dithionite by digestion in a closed vessel with sulphur. Evaporated to a syrupy consistence, and exposed for a long time to the air, sulphuret of zinc is precipitated, and the solution contains trithionate of zinc.

Nitrate of Zinc, ZnO,NO_5.—Zinc dissolves in nitric acid, and the solution, concentrated to the consistence of a syrup, lets fall deliquescent prisms, soluble in alcohol, having the form ZnO,NO_5+6HO. Three parts of water are expelled by heat, and when farther heat is applied, water and acid pass off, leaving basic salts.

Phosphate of Zinc, $2ZnO,PO_5$.—Phosphate of soda added to sulphate of zinc, throws down this salt as a white insoluble powder, which, dissolved in phosphoric acid, becomes an acid salt. The basic salt, $3ZnO,PO_5+2HO$, is gelatinous, becoming granular, and is obtained by adding basic phosphate of soda or ammonia to a solution of sulphate of zinc. Both phosphates fuse to a clear glass. It forms double salts with ammonia.

The *phosphite* is white, and somewhat soluble. The *hypophosphite* is very soluble, and difficult to crystallize.

Perchlorate of Zinc, ZnO,ClO_7.—Silico-fluoride of zinc and perchlorate of potassa, mixed, form this salt, which is deliques-

cent and crystallizable. The *chlorate* is similarly obtained from chlorate of potassa. The *hypochlorite* is formed by the direct action of hypochlorous acid on hydrated oxide or carbonate of zinc.

The *Bromate* is obtained in like manner, and the *iodate* by mixing equivalents of sulphate of zinc and iodate of soda. Both form double salts with ammonia.

Carbonate of Zinc, ZnO,CO_2.—This salt is found native as calamine. The precipitate from mixed solutions of sulphate of zinc and carbonated alkali, is a mixed carbonate and hydrate ($ZnO,CO_2+ZnO+3HO$), and ($2(ZnO,CO_2)+3ZnO+3HO$), and probably others. Wöhler obtained it in crystals by exposing a solution of oxide of zinc in carbonate of potassa to the air. Kane declares this to be a double carbonate. Double salts are formed with soda and ammonia.

Borate of Zinc fuses to a yellow glass. Its formula is $ZnO,2BO_3$. Silicate of zinc occurs native, mixed with carbonate, as electric calamine.

CHAPTER VI.

TIN.

This metal was known to the ancients, who obtained it chiefly, if not exclusively, from Cornwall. It is mentioned by Moses, and the Phœnicians are supposed to have obtained it from the Cornish mines, at least five hundred years before the Christian era.

It occurs native in two forms, the oxide and the sulphuret. The oxide is found in granite and porphyry rocks, in veins and beds, and in alluvial deposits, in small rounded grains. The latter variety of tin is called *stream tin*, and is a very pure oxide. The purest *grain tin* is obtained from it. The sulphuret, or tin pyrites, is not important as a working ore, the oxide, or tinstone, alone having been found in sufficient quantity for metal-

lurgic purposes. Its principal localities are Cornwall, Bohemia, Saxony, Malacca, and Banca.

The crude ores are crushed and washed to a certain degree of richness, and a rough assay is taken by reducing the ore in a crucible with coal broken finely. This imperfect operation is necessary to give the smelter an idea of the yield of the ore in the large way. The ores are roasted in order to drive off sulphur and arsenic, which are collected in chambers arranged for their reception. As copper pyrites is often contained in tin ores, the roasted ore is thrown into vats, which are stirred up with wooden rakes. The sulphate of copper, formed in the roasting, is thus dissolved out. It is subsequently precipitated by means of metallic iron, and all the copper thus obtained.

The ores are reduced in two ways, by the reverberatory and the blast furnaces. When the first of these is used, the ore is mixed with coal and a little slacked lime. The heat is low at first, to prevent the formation of an enamel with the oxide of tin, and is very gradually raised, the doors being all closed. The doors are thrown open after 6 or 8 hours' fusion, the bath stirred up to complete the separation of the tin, and the scoriæ raked. The uppermost of these, about three-fourths of the whole, are poor, and are thrown away. Those next below are stamped, and those resting immediately upon the surface of the metal are directly fused again for grain tin. The metal is run out into pig.

The process of refining consists of two distinct operations, *liquation* and *refining proper*. The metals combined with tin are principally copper, iron, arsenic, and tungsten, with some sulphurets and arseniurets that have not been oxidated, some unreduced oxides, and unfused earthy matters.

Liquation is accomplished by laying the blocks of metal on the hearth of a reverberatory furnace, and raising the temperature to the melting point of tin. This metal is sweated out from the pores and runs into the proper refining basin, leaving a highly ferruginous alloy. Fresh tin blocks are placed on the last, and the liquation continued till the refining basin is full.

Billets of green wood are now plunged into the tin-bath, and the gas disengaged from them produces a violent ebullition. A

froth, composed chiefly of the oxides of tin and of the foreign metals, rises to the surface, and is skimmed off and returned continually to the furnace. When the refining is supposed to be accomplished, the billets are lifted out, and the metals suffered to arrange themselves in the order of their specific gravity. Three zones or layers of metal are found, the lowest of which is full of impurities, that above is much better, and the upper one nearly pure tin. The settling being complete, the metal is ladled out. That from the bottom is so impure that it must be refined anew, as if it had been just taken from the ore. The operation of *tossing* is sometimes substituted for this. It consists in lifting up the melted metal in a ladle and letting it fall again, so as to agitate the whole mass. The froth is skimmed off, and the metal allowed to settle as before.

The residuary blocks of the liquation are now fused at a higher heat, and an impure metal is run off and allowed to settle. The upper portions are subjected to a second refining, the lower are too impure for use.

Reduction by the *blast furnace* is used for the finest varieties of commercial tin. The stream tin is usually selected. It is carefully picked and well stamped and washed. It is mixed with slags and scoriæ and smelted with wood charcoal. The fused metal is run first into a receiving basin, where it is allowed to settle for a time, when the upper layer of metal is transferred to the refining basin, and the lower sent back to the furnace.

Refined tin is the name given to the upper layer of metal resulting from the refining process. *Block tin* is the second class metal. *Grain tin* is made by heating a block till it gets brittle, and then letting it fall from a height, when it breaks up into numerous grains or tears.

TIN AND ITS NON-SALINE COMPOUNDS.

Commercial tin almost always contains impurities. These may be got rid of by a plan resembling the refining of tin already described. The metal may be kept fused for some time till the separation of the strata and the subsidence of the heavier

and impure alloys takes place, or it may be stirred to oxidate the combined metals with a portion of the tin; or, last and best, it may be converted into oxide by the action of nitric acid, washed with muriatic acid and water, and reduced with carbon.

It is a brilliant white metal, resembling silver in color and lustre, tarnishing slowly in the air. Its hardness is intermediate between lead and gold. It is very malleable, and may be hammered out into foil, the leaves of which do not exceed the thousandth part of an inch in thickness. It has an unpleasant taste, and a peculiar odor. It is soft and inelastic, and, in small bars flexible, the bending being accompanied by a peculiar sound, called the *cry* of *tin*, which has been attributed to the sliding of the crystalline particles over each other. Dipped in a solution of chloride of gold, it blackens without disengagement of gas, while zinc blackens with evolution of gas, and lead remains unchanged. It fuses at from 440° to 446°; boils at a white heat, and burns with a blue flame to binoxide. At a lower heat it forms on the surface a dross of mixed oxides.

Its equivalent on the hydrogen scale is 58.82; on the oxygen scale, 735.294. Its symbol is Sn, from the Latin *Stannum*.

Protoxide of Tin, Sn,O. 64.82.—The protochloride yields, by precipitation with carbonate of soda, a hydrated oxide of tin, which is best dried in a tube through which a stream of carbonic acid gas is passed. It is better formed in the dry way, by evaporating to dryness and then fusing crystallized chloride of tin, mixing the residue with carbonate of soda in the proportion of 3 to 2, fusing and stirring the mixture till it is entirely black, and then dissolving out the resulting chloride of sodium with water.

It is a nearly black powder, of specific gravity 6.666. It is dissolved in the acids and the pure fixed alkalies. Caustic potash, boiled on it, makes it crystalline, and dissolves a portion of it as binoxide. The alkaline solutions, kept for any length of time, deposit metallic tin, while deutoxide remains in solution.

Its salts are generally colorless or yellowish, with acid reaction and unpleasant metallic taste. They are extremely prone to absorb oxygen from the air and from other substances which yield oxygen readily, and their use in calico printing depends

very much upon this property. Zinc and cadmium precipitate the metal from the salts except from the acetate. Sulphuretted hydrogen and hydrosulphuret of ammonium throw down a brown protosulphuret of tin. This reaction shows one part of tin in 120,000 of water. Iodide of potassium throws down yellow iodide of tin, passing occasionally into red. Croconate of potassa and tincture of galls give yellow precipitates, other reagents white.

Binoxide of Tin, SnO_2. 72.82. *Stannic Acid.*—This oxide is most conveniently produced by acting upon metallic tin with nitric acid. The concentrated acid does not produce any effect, so that it must be diluted with water. The hydrated oxide, thus obtained, is white, and must be edulcorated with water, and heated to redness, when all the water is driven off, and the anhydrous binoxide is left of a fine straw yellow color. The bichloride, precipitated by an alkali and an alkaline carbonate, gives an oxide which differs widely in its properties from that which is obtained by the action of nitric acid on the metal. Thus, it is slightly soluble in nitric acid, while the other is insoluble; it is soluble in hydrochloric acid, and does not precipitate when the solution is boiled, while the other is scarcely soluble in it, but combines with it to form a salt, insoluble in hydrochloric acid, and when the acid is poured off and the residue washed with a little water, it dissolves, and again precipitates on boiling and by the addition of hydrochloric acid. Both oxides form salts with the alkalies, which are called *stannates*. The hydrate of the oxide formed by the alkali is SnO_2+2HO; that of the first described oxide, SnO_2+HO.

The salts are colorless or yellow, with an acid reaction when soluble. Cadmium and zinc throw down tin in a dendritic form from their solutions. Sulphuretted hydrogen gives a yellow precipitate, soluble in alkalies and sulphuret of ammonium. Infusion of galls and ferrocyanide of potassium produce a yellow jelly; the other reagents give generally white precipitates.

Sesquioxide of Tin, Sn_2O_3.—Fuchs obtained this oxide by treating freshly precipitated hydrated sesquioxide of iron with protochloride of tin. An exchange of elements takes place, and the sesquioxide falls as a slimy gray matter, a little yellow from the

admixture of iron. Berzelius used a saturated solution of the hydrated sesquioxide of iron in hydrochloric acid. Others have recommended adding ammonia to the two solutions before mixing them.

It dries to yellow translucent grains, soluble in ammonia. This oxide is soluble in hydrochloric acid, and then forms with terchloride of gold the purple of Cassius already described.

Protosulphuret of Tin, SnS.—Melted tin poured on its own weight of sulphur and stirred rapidly with a stick during the action, produces this sulphuret. Some tin escapes sulphuration by the rapid escape of the more volatile element. The mass is therefore reduced to powder, mixed with its weight of sulphur and projected in successive portions into a hot Hessian crucible and heated to redness.

It is a brittle compound, of a bluish-gray, nearly black color, and metallic lustre, fusing at a red heat, and acquiring a lamellated structure on cooling. It is easily reduced to metal by heating with cyanide of potassium, and dissolves in hydrochloric acid with the evolution of sulphuretted hydrogen.

Sesquisulphuret of Tin, Sn_2S_3.—The protosulphuret of tin in fine powder is mixed with flowers of sulphur and heated to redness till no more sulphur escapes. It is a deep grayish-yellow substance, with a metallic lustre. Potassa dissolves out bisulphuret, and hydrochloric acid, protosulphuret.

Bisulphuret of Tin, SnS_2.—This substance, which was formerly called mosaic gold, is obtained by heating a mixture of 2 parts of the binoxide of tin, 2 of sulphur, and 1 of sal ammoniac, at a low red heat till no more sulphur is evolved. A mixture of 4 parts of tin filings, 3 of sulphur, and 2 sal ammoniac, has also been used. It is also obtained by precipitating salts of the binoxide of tin by means of sulphuretted hydrogen, as a dirty yellow hydrate, which dries up to dark yellow hard lumps.

When the operation has been successful, the compound is procured in gold yellow scales, sometimes in six-sided tables, of a metallic lustre, a soft consistence and a soapy feel. It is soluble in pure potassa and in its carbonates at a boiling temperature, and very readily in nitro-hydrochloric acid. It forms, with me-

tallic sulphurets, double salts, which have been called sulphostannates.

Phosphuret of Tin, SnP.—Phosphorus, thrown on melted tin, gives rise to a silver white compound of a crystalline structure. Rose obtained a terphosphuret by acting on protochloride with phosphuretted hydrogen.

ALLOYS OF TIN.

The effect of alloying the noble metals with tin has already been described, as have also been the alloys of this metal with copper.

The common tin-plate is a superficial alloy of iron and tin coated with excess of tin. The iron to be used in tinning is very carefully prepared by heating, scaling off the oxide, cold-rolling and pickling in dilute sulphuric acid, till it gets an even, smooth, and perfectly clean surface. It is then dipped first in melted tallow and afterwards into a pot of melted tin, where it is allowed to remain till it is covered with a coat of the metal. This is partly drained off and partly melted off in a second pot full of grain tin. The cleansing is completed by brushing. Another dip into melted tin is then given the plates, and they are transferred into a grease-pot. The rim of tin at the edge of the plate, left after the draining, is melted off, and the manufacture is complete.

A preparation of tin-plate with a crystalline surface was much admired and extensively manufactured some years since. The superficial layer of tin was dissolved off of common tin-plate by means of dilute acid, and the exposed surface exhibited these brilliant spangles.

Pewter is essentially an alloy of tin and lead, to which copper and antimony, in varying proportions, are often added. Too large a quantity of lead will prove highly injurious by the facility with which this metal is dissolved in vinegar or acescent wines, and the poisonous character of its salts. On this account, the French government, after appointing Fourcroy, Vauquelin, and other eminent chemists, to examine into the matter, passed a law prohibiting pewterers to use more than 18 per cent. of lead in their wares.

Queen's metal is a fine variety of pewter, composed of 9 parts of tin, 1 of antimony, 1 of bismuth, and 1 of lead. *Britannia metal* is an alloy, which, for most household articles, has almost entirely superseded pewter. It is made, according to some authorities, of 2 parts of copper, 2 of brass, 1 of iron, 6 of antimony, and 89 of tin. It is a composition, however, which varies much in different workshops. *Music metal* is made of 80 parts of tin and 20 of antimony. Soft solder is a mixture of lead and tin in the proportion 67 to 33.

An amalgam of tin and mercury is the compound used for silvering mirrors. Tinfoil is spread on a marble table, and saturated with liquid mercury. A large quantity of the latter metal is then put on, a clean glass laid flat upon it, and pressed down by heavy weights. The excess of mercury being now drained off, the silvering is complete.

HALOID SALTS.

Protochloride of Tin, SnCl.—The anhydrous salt is obtained by distilling a mixture of equal parts of tin filings and corrosive sublimate, or by transmitting hydrochloric acid gas over metallic tin heated in a glass tube. It is a gray solid, with a resinous lustre, which fuses below redness and sublimes at a high temperature. It may be obtained in crystals by dissolving tin in hydrochloric acid, and evaporating the solution. It is necessary to have excess of metal present in order to insure the formation of a protochloride. The crystals are long, colorless prisms, and have the form SnCl+HO.

Dissolved in water, a cloudiness of greater or less density appears, owing either to the air contained in the water or to a portion of oxychloride of tin. Hydrochloric acid clears the solution. The chloride is an excellent reducing agent, and is used in analysis to reduce the various metallic oxides to metal, or to a lower degree of oxidation. It forms double salts with the alkalies and alkaline earths.

Sesquichloride of Tin, Sn_2Cl_3.—This has been sufficiently described under the head of *Purple of Cassius*, in the chapter on Gold.

Bichloride of Tin, $SnCl_2$.—When protochloride of tin is heated in chlorine gas, or when a mixture of 8 parts of granulated tin and 24 parts of corrosive sublimate is distilled, a singular liquid, called the *fuming liquor of Libavius*, passes over. It is a volatile, colorless liquid, which, when exposed, emits dense white fumes, owing to the moisture it attracts from the atmosphere. It remains fluid at 28° below Fahrenheit's zero, and boils at 248°, giving off a vapor, the specific gravity of which, according to Dumas, is 9.1997. With one-third its weight of water, it congeals to a solid mass of crystals; in more water, it dissolves. Solution of tin in *aqua regia* furnishes the same crystals. It forms double salts with the alkaline chlorides. The *pink salt* of the color-printer is one of these. It is made by adding sal ammoniac to a solution of the bichloride, and crystallizing. It forms several compounds with sulphur.

Bromide of Tin is a white soluble salt. The bi-bromide, formed from tin and bromine, is fusible, soluble in water, and sublimes unchanged.

Iodide of Tin, formed when iodine and tin are heated together, is a brownish-red, fusible and soluble salt. It sublimes at a high heat. It forms double salts with the alkaline iodides. Dry protochloride of tin mixed with chloride of iodine, gives rise to a bichloriodide of tin, which separates in orange-colored crystals. The biniodide is obtained in yellow crystals, by treating the hydrated oxide with hydriodic acid. Water decomposes it.

OXYSALTS.

Sulphate of Protoxide of Tin, SnO,SO_3.—When this is dissolved in sulphuric acid, slightly diluted with water, there results a saline mass, which dissolves in boiling water, and crystallizes on cooling. *Sulphite of tin* is a white insoluble powder, which subsides when sulphite of soda is added to chloride of tin. Sulphurous acid dissolves tin with the simultaneous formation of hyposulphite and sulphuret.

Sulphate of Binoxide of Tin, $SnO_2,2SO_3$.—Tin filings, dissolved in three times their weight of boiling oil of vitriol, form a sulphate of the binoxide.

Nitrate of Tin, SnO,NO_5.—This salt is obtained in solution by treating the hydrated oxide with cold nitric acid. The action of nitric acid on metallic tin induces decomposition not only of the water, but of the acid, as is proved by the resulting compound, which contains not only nitric acid but ammonia also. *Nitrate of the binoxide* is obtained by dissolving the hydrated binoxide in cold nitric acid.

Phosphate of Tin, $2SnO,PO_5$.—Phosphate of soda precipitates this salt from a solution of tin. It is white and fusible to a glass. The *phosphite* is a white powder, which, when dissolved in hydrochloric acid, is a most powerful reducing agent.

Borate of Tin is white, insoluble, and fuses to an opaque glass.

The other salts of tin are of no particular interest.

CHAPTER VII.

LEAD.

Lead is one of the most anciently known metals. It is mentioned in the Pentateuch. In alchemical language it is called saturnum, from its planet, Saturn. The most common ore is *Galena*, the sulphuret of the metal.

METALLURGY OF LEAD.

Lead is so fusible and so easily reduced, that the rudest contrivance will secure a paying yield from rich ore. In the great lead region of the West, the early settlers made a heap of wood and ore, set fire to it, and collected the metal, in pigs, in little trenches dug in the earth. It is usually reduced in low blast furnaces or reverberatories. The former furnace is objectionable on account of the great loss of lead, amounting sometimes to nearly half the metal contained in an ore. It is chiefly used for the reduction of rich slags, carbonate of lead, and litharge.

In the reverberatory furnace, the ore is spread upon the

hearth and repeatedly stirred, while a low red heat is given to the mass. Sulphur slowly burns off, leaving behind oxide of lead, while some of the sulphuret is oxidated to a sulphate and there remains some unaltered galena. The roasting being completed, the heat is raised, and the lead which sweats out is received in an iron pot. After the liquation is ended, the dross and cinder are raked together, and a fresh charge operated on in the same manner. The freshly added galena forms, with the oxide of lead, sulphurous acid, metallic lead, and a portion of subsulphuret, and the oxide, reacting on the sulphate, produces a subsulphate.

The cinder and dross are now spread over the hearth; coal is mixed with it, and a higher heat applied. The sulphate, oxide, and sulphuret are partially reduced, and metal flows out. Lime is then added, which forms sulphuret of lime with galena, liberating metal, and, with the sulphate, oxide of lead, which is reduced by the coal, while, by combining with the silica, it sets free any plumbeous oxide which might have existed originally in the ore as a silicate, or have been formed by the previous operations. These processes are repeated till the slags are incapable of farther reduction in this way. The richer the ores are, the less lead is lost in this process. It sometimes amounts to but 2 per cent. The rich slags are reduced in a blast furnace.

Poor ores and carbonates are commonly reduced in low blast furnaces. The sulphurets are roasted and mixed with lime and oxide of iron, the latter of which is essential to the production of a fusible slag. Iron is often used for the direct reduction of galena, in either of the furnaces. It forms the fusible sulphuret of iron, and liberates lead. The favorite method of dry assay of lead ore depends upon this property of iron. The necessary amount of alkali to decompose the silicious matters of the ore, and to form a slag with them and the oxides, is mixed with the powdered ore, and beaten down around iron nails, previously arranged in the crucible. Heat is then applied, and when the contents are in a state of fusion, the nails are lifted one by one, rinsed in the slag, and withdrawn. The metal collects at the bottom.

LEAD AND ITS NON-SALINE COMPOUNDS.

Lead.—Obtained by the above methods, lead is always more or less impure. It frequently contains copper, zinc, arsenic, &c., but the most common foreign ingredient is silver. There is little commercial lead free from this, though there is scarcely any which contains enough of it to pay the cost of extraction, the separation of these two metals being now so well understood by the smelters. The most convenient way of obtaining it free from the common impurities of copper and silver, is to dissolve it in nitric acid, and precipitate with excess of ammonia, which dissolves the oxides of the two latter metals, and to reduce the ignited oxide with black flux. Iron can easily be separated by precipitation with hydrochloric acid. The pure oxalate, when ignited, furnishes a lead entirely free from carbon.

Lead is a bluish-gray metal, with a high lustre when first fused or cut, but rapidly tarnishing in the air. It crystallizes in regular octahedra. Under water, it forms hydrated oxides, which are soluble in water, and poisonous. The best safeguard against them is a notable quantity of sulphates or phosphates in the water, which form with the lead an insoluble coating over the inside of the pipe, thus protecting it from farther oxidation. Persons using water conveyed through lead pipes, have been seriously, and even fatally affected by neglecting these precautions. The change is due to the air contained in the water, as recently boiled distilled water has no effect upon the metal.

At high temperatures, lead absorbs oxygen with great rapidity. Fused in open vessels, a gray film of protoxide and metallic lead is formed; and, when strongly heated, it is dissipated in fumes of protoxide. Cold sulphuric acid has no effect upon it, but, when heated, oil of vitriol acts on it slowly. It fuses at about 612°, and crystallizes when slowly cooled.

The symbol of lead (plumbum) is Pb, its equivalent 103.76 on the hydrogen, 1294.5 on the oxygen scale. Its specific gravity is 11.33 to 11.445.

Dinoxide of Lead, Pb_2O.—This is a dark gray, nearly black compound, formed by heating dry oxalate of lead to low redness.

The acid and part of the oxide are decomposed into carbonic acid and carbonic oxide, which pass over.

Protoxide of Lead, PbO.—This is obtained pure by heating nitrate of lead to redness. In the large way, it is made by calcining refuse lead at 600°, and as an incidental product of cupellation. Fused litharge slowly cooled crystallizes. Crystals may also be obtained from the solution in caustic alkali.

It is red when hot, changing when cool into a yellow powder, with an orange cast. The hydrated oxide is white and crystalline.

The salts of lead, except with colored acids, are colorless. They are precipitated by zinc, as metal, in an arborescent form, and as black or brown sulphurets by sulphuretted hydrogen. The alkalies throw down white hydrated oxide, and the carbonates white carbonate. The characteristic tests for lead are chromate of potassa and iodide of potassium, both of which throw down yellow precipitates.

Red Lead.—This is a compound about the composition of which there has been much difference of opinion among chemists. It was formerly regarded as a sesquioxide, but now as a mixture of two oxides, occurring either as $PbO+PbO_2$, or $2PbO+PbO_2$. Minium, or red lead, is obtained by protracted calcination of the metal. Its varying color depends partly on the mode of its preparation, partly on the admixture of foreign ingredients.

Peroxide of Lead, PbO_2.—This oxide, which has been called plumbic acid, may be obtained by boiling dilute nitric acid on red lead. The acid dissolves the protoxide, leaving the peroxide. It unites with alkalies to form soluble salts.

Red lead is used in the manufacture of glass, and the peroxide as an oxidizing agent in organic chemistry, and, in the arts, to make lucifer matches more inflammable. Litharge is extensively employed as a drier in varnishes and paints, and, by the apothecary, in the preparation of his lead plaster, the basis of all his plasters.

Sulphuret of Lead, PbS.—This substance is found native as *galena*. It is formed by fusing lead with sulphur, or by precipitating it from its solutions by means of sulphuretted hydro-

gen. In the former instance, it is lead gray with a metallic lustre; in the latter, dark brown or black, and earthy looking.

It fuses readily, and at a high heat vaporizes. By calcination, part of the sulphur is burnt off, and lead and sulphate of lead remain. Heated to whiteness with charcoal, it becomes a subsulphuret, which is resolved by heat into galena and metal. It is partially decomposed by steam into sulphuretted hydrogen and lead. Dilute nitric acid dissolves it, leaving sulphur; strong acid converts it into a sulphate. Even dilute acid, at a high heat, has often the same effect, so that it is best to dissolve the galena at the common temperature of the air. Iron, ignited with it, forms sulphuret of iron, leaving metallic lead. The dry assay is made in this way, but as it is always, even in the best hands, attended by a loss, it is best to rely upon the humid assay.

Phosphuret of lead, made by throwing phosphorus on the melted metal, resembles lead in appearance, but is not malleable.

ALLOYS OF LEAD.

Shot are made of an alloy of a large proportion of lead with a little *arsenic*. One of the English patents prescribes a ton of the former to 40 pounds of the latter. *Antimony* added to lead, in the proportion of 1 to 4 or 5, hardens it, and constitutes the ordinary type-metal. Lassaigne's formula (lead, 2; copper, 1; antimony, 1) is better, and gives clearer type, because copper makes an expanding alloy with lead. A small quantity of *bismuth* makes lead tougher; equal parts of the two metals form a brittle alloy. The alloy of *tin* with lead has already been described in the chapter on tin. Rose's *fusible metal* is 2 parts of bismuth, 1 part of lead, and 1 part of tin. A little *mercury* added to this lowers its fusing point. *Mercury* forms with lead a solid crystalline amalgam, which floats in the liquid mercury. This metal may be transferred from one vessel to another, by means of a lead rod bent into the form of a siphon. The lead is penetrated by the mercury, but remains malleable, and the crystalline amalgam is carried over. With *gold* and the *platinoid metals*, as well as with *copper*, lead forms brittle alloys.

Lead is used by the dentist for his antagonizing models in making plate-work. At first it is not alloyed, but gradually, during the process of working, it becomes contaminated with scraps of zinc, bismuth, &c., which harden it. An alloy of copper and lead would be preferable to lead alone, because it expands during cooling, and consequently receives a more accurate impression than the pure metal. Bismuth, zinc, and antimony alloyed with lead cause it to contract on cooling, and are therefore, unless counteracted by copper, undesirable contaminations.

HALOID SALTS.

Chloride of Lead, PbCl.—This salt is easily formed by precipitating a solution of lead in nitric acid, by means of hydrochloric acid or a soluble chloride. It is a heavy crystalline white powder, which may be dissolved in boiling water, out of solution in which it crystallizes, on cooling, in brilliant, transparent, acicular crystals, often with a yellowish tinge. In the air it is volatilized, leaving oxychloride of lead (PbO + PbCl). Another oxychloride is formed by precipitating subacetate of lead with common salt, and driving off water by heat. Turner's patent yellow is an oxychloride made in this manner, and rendered yellow by fusion.

Bromide of lead (PbBr), is a white crystalline powder, fusible to a red liquid, made either by double decomposition or direct action.

Iodide of lead (PbI) is obtained in beautiful crystalline scales, of a golden yellow color, and obscure metallic lustre, by precipitating a solution of nitrate of lead with iodide of potassium. Dilute solutions give the finest crystals. A solution of 1 part of iodide of potassium in 10 of water, to which iodine is added till it becomes yellowish-brown, is said to furnish the best results, when a dilute lead solution is poured into it. This salt is soluble in 1,235 parts of cold and 190 parts of boiling water.

Fluoride of lead is a white, amorphous powder, almost insoluble in water, formed by treating the oxide or carbonate with hydrofluoric acid.

OXYSALTS.

Carbonate of Lead, PbO,CO_2.—This salt occurs native, both amorphous and in beautiful transparent crystals. The artificial compound is made by various formulæ, and is very extensively used as a pigment. The neutral salt, the formula of which is given above, is obtained by precipitating nitrate of lead with an alkaline carbonate.

An imperfect pigment, with little body and inferior whiteness, is made by exposing the finely divided metal to air alone, or air and carbonic acid, with constant agitation. Thenard's process furnishes a paint of less body but more brilliant whiteness than the ordinary white lead. He obtained the carbonate by precipitating the basic acetate by a stream of carbonic acid gas passed through the solution. By another process, sheets of lead are hung up in a room, and exposed to the conjoined action of vapor of vinegar, steam, and carbonic acid. The celebrated Kremnitz white is made by suspending sheets of lead in a trough, at the bottom of which is a fermenting mass of wine lees, vinegar, &c., which sends up vapors of vinegar and carbonic acid, thus corroding the lead. The high reputation of this pigment is due partly to the very careful manner in which it is elutriated and prepared for the market, and partly to the great purity of the metal from which it is made.

White lead, well prepared, has a soft velvety feel when rubbed between the fingers. It is said to consist of globules of from 0.00001 to 0.00004 of an inch in diameter. When prepared in the wet way, these are larger and of a more crystalline character. In commerce, it is adulterated with sulphate of baryta, sometimes to a very great extent. Some specimens of commercial white lead contain as much as 75 per cent. of this adulteration. It has been thought that, while the baryta salt diminishes the body of the pigment, its presence is attended with some advantages, among which is a diminished tendency to change of color.

The following formulæ of different specimens have been given: $3(PbO,CO_2)$ and PbO,HO; $2(PbO,CO_2)$ and PbO,HO; PbO,CO_2+PbO,HO. The last formula represents the better class of commercial white lead.

Nitrate of Lead, PbO,No_5.—When lead is heated with dilute nitric acid it is rapidly taken up, and the solution, after evaporation and cooling, lets fall crystals belonging to the regular system. It is soluble in water, less so in nitric acid, not at all in alcohol.

Sulphate of Lead, PbO,SO_3.—Sulphuric acid acts upon lead with such difficulty that this metal is universally used by the manufacturers of oil of vitriol in the construction of their condensing chambers and concentration-vats. It is not, however, wholly insoluble in this acid, as little or no commercial oil of vitriol can be found destitute of a notable quantity of the salt. It is best obtained by precipitating the nitrate or acetate of lead with sulphuric acid or a soluble sulphate.

It is a white powder, fusible without decomposition, but readily decomposed by ignition with charcoal or silica. It is scarcely soluble in water, but dissolves in small quantity in water acidulated with sulphuric acid, and more freely in oil of vitriol. It is soluble in ammoniacal salts, especially the sulphate, with which it forms a double salt.

Phosphate of Lead.—There are two phosphates of lead formed by precipitating solutions of lead salts with the common phosphate of soda. One of these is obtained from the acetate, the other from the chloride of lead. Both are sometimes formed together. The latter fuses into a yellow bead, which, on cooling, acquires crystalline facets.

Acetates of Lead.—There are four acetates of lead. The *neutral acetate* (PbO,A,3ag) is obtained by dissolving the oxide or carbonate in excess of acid and crystallizing. When the solution is rapidly cooled, needles are deposited. By slower refrigeration, white right-rhombic prisms, with dihedral summits, are obtained. It is the salt known as sugar of lead, and is largely used in medicine and in the arts. The *sesquibasic acetate* (3PbO,2A) is made by gently heating the dry neutral acetate in a porcelain capsule, till the fused salt congeals to a porous white mass. This is then dissolved in water, the solution concentrated to the consistence of syrup and set aside to cool, when pearly, six-sided tables separate. The *tribasic acetate* (3PbO,A) is deposited in long silky needles from a cold

saturated solution of neutral acetate which has been mixed with one-fifth of its volume of water of ammonia. The *sex-basic acetate* (6PbO,A) is a white powder, which, under the microscope, is found to be crystalline. It is obtained by super-saturating any of the acetates with ammonia. Boiling water dissolves it and lets it fall, on cooling, in brilliant, feathery crystals. The basic acetates are used in dyeing, and in the manufacture of chrome yellow.

Borate of Lead.—Lead forms, with boracic acid, glasses of various degrees of hardness and solubility. A very soft yellow glass is obtained by fusing together 112 parts of oxide of lead and 24 of boracic acid. A hard, transparent, and highly refracting glass is made from the same quantity of litharge and 72 parts of the acid. $PbO,2Bo_3$ is slightly soluble in water.

Chromate of Lead, PbO,CuO_3. 164. *Chrome Yellow.*—This is a powder formed in various ways, but usually by precipitating a solution of crystallized acetate or nitrate of lead by chromate or bichromate of potassa. It is a fine yellow pigment, insoluble in water, but soluble in potassa, with a formation of the basic chromate. Various paler lemon tints are obtained by mixing sulphuric acid, in different proportions, with the chromate of potassa before the precipitation. They depend upon the admixture of the white sulphate of lead, which weakens the yellow.

Basic Chromate of Lead, $2PbO,CrO_3$. 276. *Chrome Orange.*—This is easily made by boiling the yellow chromate with weak *aqua potassæ*. Hayes obtained it in orange yellow needles, by treating a solution of litharge in caustic soda with chromate of potassa, in an atmosphere charged with carbonic acid. Nohler and Liebig made a fine vermilion-colored basic chromate, by projecting the yellow chromate in nitre fused at a low heat, till the latter salt is almost entirely decomposed. The crucible is allowed to stand till the dense basic salt subsides, when the fluid part is poured off, and the basic salt washed rapidly with water. Chrome orange is also used as a pigment, but is more liable to fade in the air than the yellow.

Silicate of Lead is the basis of flint glass and artificial gems. Strass is said to be $KO,SiO_3+3(PbO,SiO_3)$.

CHAPTER VIII.

BISMUTH.

Bismuth was first shown, by G. Agricola, to be distinct from lead, in 1546. It is occasionally found native, but most commonly combined with the ores of other metals, with sulphur, selenium, tellurium, and silica. In Saxony, where it is principally worked, it is obtained as a secondary product from arsenical cobalt.

At Schneeberg, in Saxony, it is sweated out of the ore in peculiar eliquation furnaces. The broken ore is put into earthen pipes which have holes in their under side, to allow the melted metal to drip out into hot iron pans. These contain coal-dust, which is floated up by the melted metal, and forms a film on its surface, protecting it from oxidation. When the pans are nearly full, the metal is lifted out and cast in bars.

Bismuth thus obtained resembles the pure metal, but is largely contaminated with arsenic, sulphur, iron, &c.

BISMUTH AND ITS NON-SALINE COMPOUNDS.

Bismuth.—The commercial metal is best purified by dissolving in pure nitric acid, filtering or decanting, to get a clear solution, precipitating the subnitrate by the addition of water, digesting the precipitate with caustic potassa to extract arsenious acid, and reducing the residue with black flux at a low red heat.

It crystallizes in octahedra and cubes, with distinct cleavage. It is best crystallized by heating the commercial metal in a crucible with a little nitre, to the fusion point of the salt. More nitre, in small quantities, is added from time to time, the whole being constantly stirred. Test pieces are taken out repeatedly for examination. At first, they are of a violet or rose color, which disappears on cooling. When this tint disappears and is replaced by a green or yellow, which is permanent, the metal is

sufficiently purified. It is then to be poured into a heated crucible, cooled till about one-half congealed, the surface broken, and the remaining liquid metal poured out.

It is a soft metal, with but little sonorous property, brittle, but capable of some degree of extension by careful hammering. Its malleability is increased by heating. It is reddish-white, with some lustre, and undergoes little change in the air at common temperatures, but, when fused in open vessels, becomes coated with a gray film of mixed metal and oxide. It fuses at about 500°, and is said to expand on cooling. At a high heat it may be distilled in close vessels, being condensed, after sublimation, in laminæ. It is soluble in nitric acid and aqua regia, but the process is immediately arrested by laying a piece of platinum on the metallic bismuth.

The specific gravity of pure bismuth is 9.654 according to some authors, 9.799 according to others. The symbol of bismuth is Bi. Its equivalent is variously stated, as the opinions of chemists vary, in reference to the constitution of the most powerful base. This was formerly regarded as a sesquioxide (Bi_2O_3), and, the percentage being about 89.87 bismuth, and 10.13 oxygen, the combining number was stated at 106.5. After a time, however, an analogy was discovered between the salts of bismuth and those of magnesia. The formula was consequently altered to BiO, and the equivalent to 71. Again, the resemblance between compounds of bismuth and antimony, and the analogy between the specific volumes of bismuth and tin, led to the adoption of BiO_3 as the formula, and consequently 213 as the atomic weight of the metal.

Suboxide of Bismuth.—This oxide is formed when bismuth is melted in the air, and kept fused for a long time, or when the basic nitrate is digested with excess of protochloride of tin. It is reddish-brown or black, according to the mode of preparation.

Oxide of Bismuth.—Bismuth, heated in the air, burns with a pale blue flame to oxide or flower of bismuth. In the dry way, this oxide is prepared by the thorough oxidation of fused bismuth by constant stirring, or by igniting the carbonate or nitrate. Thus obtained, it is a yellow powder. It may be

procured in shining yellow needles by fusing caustic potassa with excess of the oxide, and boiling with a concentrated potash or soda lye. The hydrate is white, and is made by double decomposition.

Bismuthic Acid.—Some experiments are recorded which go to show that there are other oxides, some of which appear to have slight acid properties. By fusing the oxide with caustic soda, boiling the fused mass with soda lye, and washing with nitric acid and water, a brown oxide is obtained, which yields a yellow oxide when fused with caustic potash. The yellow oxide, treated with nitric acid, forms another of a reddish-brown tint.

Sulphuret of Bismuth.—The tersulphuret occurs native as Bismuth Glance. It may be made by fusing the metal and sulphur together, or by precipitating bismuth with sulphuretted hydrogen. It is either lead gray or brown, according to the manner in which it is prepared.

Phosphuret of Bismuth.—Phosphorus has not a very strong affinity for bismuth. It combines with it, however, in the dry way, forming a foliated compound. It precipitates from the nitrate a black phosphuret, which loses all its phosphorus by distillation.

ALLOYS OF BISMUTH.

Bismuth increases the fusibility of an alloy, and, if added in sufficient quantity, usually confers on the compound the property of expansion. The dentist uses it to alloy his zinc for moulds, on account of the two properties above-mentioned.

It alloys readily with *potassium* and *sodium*. The former mixture may be obtained by fusing bismuth with bitartrate of potassa. These alloys are readily oxidated by water, hydrogen being given off and bismuth left in a pulverulent form.

Bismuth does not combine readily with *arsenic*, but with *antimony* it unites in every proportion, and when the alloy contains 33 or more parts of bismuth in the hundred it expands on cooling. With *copper*, it forms a red and brittle compound.

SALTS.

The salts of bismuth are easily obtained by solution of the oxide in liquid acid, by double decomposition, and by decomposition through the agency of water. All the soluble salts form basic salts on the addition of water to their solutions, unless the latter contain great excess of acid. Metallic bismuth is rapidly precipitated from them by zinc and cadmium, more slowly by tin, iron, and lead, and by copper only from a warm solution. Alkaline carbonates throw down a carbonate; earthy carbonates a hydrated oxide. Sulphuretted hydrogen and hydrosulphurets precipitate all the bismuth as a brownish-black sulphuret.

Chloride of Bismuth.—This salt, which has also been called *butter of bismuth*, is formed with evolution of light and heat, when finely divided bismuth is introduced into chlorine gas. The common mode of preparation is to distil bismuth with corrosive sublimate or to dissolve it in strong hydrochloric acid. It is brownish or grayish-white, and, when formed by the last process, crystallizes in prisms. It fuses readily to an oily liquid, and at a gentle heat is volatilized. Water decomposes it, throwing down an oxychloride. This is white, crystalline, fusible, and easily decomposed. The chloride also forms double salts with the alkaline chlorides.

Bromide of Bismuth is formed by the direct action of heated bromine upon finely-divided metallic bismuth. It is a steel gray compound, resembling iodine. At 392°, it fuses to a hyacinth red liquid, but regains its original appearance on cooling. Exposed to the air, it rapidly absorbs moisture, and acquires a fine sulphur yellow color. Water decomposes it into hydrochloric acid and oxide of bismuth.

Iodide of Bismuth is a brown crystalline salt, obtained by double decomposition. The *subiodide* is volatile, subliming, before fusion, in scales of a metallic lustre. It is made by heating together equal parts of bismuth and iodine. An oxyiodide is made by boiling the iodide in water.

Sulphate of Bismuth.—This salt is obtained by dissolving the metal in sulphuric acid and evaporating to dryness. Ignited in

hydrogen, it leaves pure bismuth. Water resolves it into sulphuric acid and an insoluble basic sulphate.

Nitrate of Bismuth.—The neutral salt is made by dissolving bismuth in warm nitric acid and crystallizing. The action is so violent that the temperature rises to actual ignition when finely divided bismuth and fuming nitric acid are used. The crystals are transparent and colorless prisms. Water forms with it the basic salt known by the various names of pearl white, trisnitrate, subnitrate, and magistery of bismuth. It is a pure white, pearly, loose powder, composed of crystalline scales invisible to the unaided eye. Sometimes minute needles are mingled with the scales. The greatest yield is obtained by adding 2,400 parts of boiling water to 100 parts of the crystals. In this way 45.5 parts of basic salt are produced.

The salt was used as a cosmetic, but has gone out of vogue on account of its growing dark by exposure to the air and blackening in the presence of sulphuretted hydrogen. It is employed in medicine, and is a favorite remedy with many physicians in cases of indigestion, especially when accompanied by much gastric pain. Some regard it as a local anæsthetic to the stomach.

Phosphate of bismuth is a white insoluble powder, fusible to a white enamel. The bibasic phosphate is formed by double decomposition with pyrophosphate of soda. The monobasic phosphate is obtained by adding metaphosphoric acid and ammonia to a salt of bismuth.

We pass over the remaining salts of this metal.

CHAPTER IX.

PLATINUM.

This metal was mentioned by Ulloa in 1741, but does not appear to have been attended to in Europe till 1748. It was first sent over from South America as platinum sand, and brought into the market under the name of white gold. The Spaniards,

however, soon gave it the name of *platina* (which is a diminutive of *plata*, silver), from its resemblance in color to that metal.

It is rarely, if ever, found pure, being alloyed with several other metals, the most common of which are those commonly called the platinoid metals, palladium, iridium, osmium, rhodium, and ruthenium. It has also been found in company with gold, silver, iron, manganese, copper, lead, titanium, and chromium.

It occurs in the form of grains, which are usually flattened, and resemble somewhat the gold *pepitas*. They are generally smaller than flaxseed, though occasionally found as large as peas. A piece brought by Humboldt from Choco, in Peru, and by him presented to the Cabinet at Berlin, is larger than a pigeon's egg, and weighs 1088.6 grains. In the Royal Museum of Madrid is another, larger than a turkey's egg, and weighing fully 2 pounds troy. But the largest masses have come from Russia. One of these, discovered in 1824 at Nischne-Tagilsk, weighed 10 pounds; and another, found in 1830, weighed fully 18 pounds avoirdupois.

The color of the grains of native platinum is generally a grayish-white, like tarnished steel. The rougher particles have often earthy and ferruginous matters clinging to them. The black oxide of iron is a very common contamination. Their specific gravity is much lower than that of the metal, varying from 15 in the smaller to 18.94 in the larger specimens. Among them are found, in very considerable quantity, the excessively hard, tough, flat, silvery spangles of iridosmin.

Of the localities of platinum, one of the most important is the western slope of the Andes, in New Granada and Peru. The gold washings of these regions contain this metal. The deposit is found in alluvial ground at the depth of about 20 feet. Formerly, the metals were separated by picking; and, when it was supposed that the platinum might be used to debase the gold, great quantities of it were thrown into the rivers. Brazil is another important platinum region. The metal is found there also mixed with small particles of gold, but without the magnetic iron-sand or small zircons which accompany the Peruvian ore. It is mixed with fibrous and radiated grains of native palladium,

and the platinum granules themselves are remarkably spongy and brilliant. In St. Domingo, this metal is found in the ferruginous quartzose sand of the river Jacky, near the mountains of Sibao. This native platinum contains nearly all the associated metals already named.

The most important source of platinum, however, is the Ural range of mountains in the empire of Russia. The geological conformation of the region producing it corresponds very much with that of the platinum region of South America. It is mingled with gold in sands which are almost all superficial, covering an argillaceous soil, and including debris of dolerites, protoxide of iron, corundum, &c. The grains are thicker, and not so flat as the Peruvian; they are round, less brilliant, and more lead-colored. The sand is manifestly the result of the wearing away of the surrounding rocks. Large quantities of iridosmin are found in it.

Though usually contained in alluvial washings, Boussingault discovered it in a sienitic rock associated with gold; and Vauquelin found 10 per cent. of it in an argentiferous copper ore, said to have come from Guadal Canal, in Spain.

PREPARATION OF PLATINUM.

The ore is first thoroughly washed, in order to free it as much as possible from earthy impurities. A magnet is then passed over it to remove the magnetic iron ore that may be present. The remainder of the iron is dissolved out by means of dilute hydrochloric acid.

The purified grains are now introduced into a tubulated retort, connected with a cooled receiver. Hydrochloric acid is then poured over them, and heat is applied; nitric acid being gradually added, not in excess, lest iridium should be precipitated. Distillation is carried on till the residue in the retort has acquired the consistence of a syrup, when it is dissolved in hot water, mixed with the distillate, and the whole distilled anew. What comes over is colorless (if not, it is distilled till it is so), and contains osmic acid. It is neutralized by ammonia, or milk of lime, charged with sulphuretted hydrogen, and allowed to stand until the sulphuret of *osmium* subsides, for which several days

are required. The addition of the alkalies is designed to prevent the decomposition of the sulphuretted hydrogen. The precipitation should be made in a closely-stopped flask, of such a size as to be nearly filled with the solution. The resulting sulphuret of osmium contains, according to Berzelius, from 50 to 52 per cent. of metal. This process depends upon the volatility of osmic acid, which is formed by the continuous decomposition of the chloride of osmium.

The residue may be again treated with *aqua regia*. It must be boiled to expel the excess of chlorine, generated by the decomposition of chloride of palladium, filtered and precipitated by an excess of saturated watery solution of chloride of potassium, which throws down the double chlorides of platinum, iridium, and ruthenium. The precipitate must now be washed with a solution of chloride of potassium, and the double chloride of *ruthenium* extracted by alcohol.

The double chlorides of platinum and iridium are dried, mixed with twice their weight of carbonate of potassa, and heated nearly to fusion, in order to decompose the double salts, and oxidate the rhodium and iridium. It is then washed, first with water, afterwards with dilute hydrochloric acid, and finally with water on a filter. The residue is then treated with slightly warm dilute *aqua regia* till nothing more is taken up. The fluid is decanted, and concentrated acid poured upon the residue; the solutions mixed and evaporated with chloride of sodium. The object of adding this is to prevent the formation of proto-chloride of platinum. The soluble double chloride is now extracted with water, and the residue, which is oxide of iridium, well washed upon a filter. The same process is used with the solutions so long as they contain iridium. The pure platinum solutions are precipitated with sal ammoniac, which throws down a brilliant yellow double salt if no foreign metal be present. The precipitate, heated to ignition and washed, is pure *platinum*. The solutions to which the sal ammoniac has been added are also evaporated and ignited, to obtain the platinum that may have escaped precipitation. The oxide of *iridium*, ignited in a stream of hydrogen gas, yields the metal.

The liquid from which the double chlorides were separated,

contains palladium, rhodium, copper, and iron, with some platinum and iridium. It is acidulated with hydrochloric acid, and precipitated by means of metallic zinc or iron. The precipitate is redissolved in *aqua regia*, and exactly neutralized with carbonate of soda. Cyanide of mercury is added, which throws down cyanide of palladium, mixed with some copper; this is again dissolved in *aqua regia*, and chloride of potassium added. The solution is evaporated to dryness, with repeated addition of *aqua regia*, and the dry residue powdered. The double chloride of copper and potassium being extracted by means of alcohol, the palladio-chloride of potassium remains. This, ignited with sal ammoniac and washed, leaves pure *palladium*.

The liquid which remains after filtering off the precipitated cyanides in the last process, is evaporated to dryness with hydrochloric acid, to expel hydrocyanic acid. The dried mass is ignited with bisulphate of potassa, and the potash salts and the copper are dissolved out with water and hydrochloric acid. The residue is heated with bisulphate of potassa till it begins to congeal. This takes up the oxide of rhodium. The salt is then treated with boiling water, and the red or black solution evaporated. The same process must be repeated so long as the salt is colored. To avoid the trouble of adding much bisulphate of potash, weighed quantities of sulphuric acid may be added, from time to time, to the decomposed salt. The residue from this is ignited with carbonate of potassa and washed. Oxide of *rhodium* remains.

The residue of the first treatment with *aqua regia* contains iridium, osmium, and iridosmin. Wöhler mixed this with common salt, introduced it into a green glass tube, and, while heated to low redness, passed a stream of chlorine gas over it. The tube communicated with a tubulated receiver containing ammonia, and the operation was continued till the chlorine entered the ammoniacal solution in considerable quantity. Two double salts are thus formed, the iridio-chloride and the osmio-chloride of sodium. The latter salt decomposes in the presence of water into osmium, hydrochloric acid, and osmic acid. The latter passes over into the receiver, while the two former combine to be again decomposed. The contents of the tube are digested in water, and the brown solution submitted to a second distillation,

to obtain more osmic acid. The remainder is evaporated in an open dish, with the occasional addition of carbonate of soda. The dry black mass is feebly ignited in a Hessian crucible. When cold, the saline matter is removed by boiling water, and there remains a black powder of oxide of iridium, which may be reduced to metal by hydrogen gas.

Ruthenium is separated by fusing equal parts of potassa and chlorate of potassa in an iron crucible, and adding 6 parts of iridosmin. The resulting black mass is washed with warm water, leaving behind oxide of iridium and unaltered iridosmin. The yellow water which has been poured off from the washing is exactly saturated with nitric acid, oxide of ruthenium falls, and osmiate of potassa remains in solution.*

The Russian process is more simple than the above (which is a modification of Berzelius's process of analysis), though it does not accomplish as perfect a separation of all the platinoid metals. The ore is treated with *aqua regia* in open vessels on a sand-bath, arranged under a glazed dome with a ventilating chimney, so that all the vapors are carried out of the laboratory. Heat is applied for eight or ten hours, till the cessation of red fumes proves that all the nitric acid is decomposed. The supernatant solution is decanted, and the residue again treated with *aqua regia* till all is taken up. The acid used is composed of 1 part nitric and 3 hydrochloric acid. It requires, of acid, from ten to fifteen times the weight of the ore to dissolve it.

The solutions thus made are all very acid, to prevent the precipitation of iridium, when water of ammonia is added. This is the next process, and the ammonio-chloride of platinum having settled, the supernatant liquid is poured off, and the precipitate well washed, dried, and calcined in platinum crucibles.

The mother waters and washings are treated separately. The first being evaporated to one-sixth of their bulk, let fall the iridium as a dark purple powder, occasionally crystallized in octahedra. The washings are evaporated to dryness, and the residue treated like fresh ore, but the platinum obtained from them needs a second purification.

The result of the ignition of the platino-chloride of ammonium

* Booth's Cyclopædia of Chemistry.

is spongy platinum. This is beaten with water in bronze mortars, sifted through fine sieves, and the powder driven forcibly into a cylinder by means of a powerful coining press. It is then turned out of the mould and baked for 36 hours in a porcelain kiln, after which it may be forged. It contracts in volume from one-sixth to one-fifth during the calcination. In very large quantities, this process is somewhat modified. The block obtained by compression is heated in a smith's forge at the angle of meeting of two tuyeres. When it has reached the welding point, which is intense whiteness, a heavy drop, very much like the hammer of a pile-driving machine, is let fall upon it. It is reheated, and receives a fresh blow every twenty minutes, and in a week or ten days its consolidation is completed.

These large masses are used for the great pans employed in making pure, concentrated sulphuric acid, and the vessels for parting by means of that acid.

METALLURGY OF THE ALLOYS OF PLATINUM.

Gold and Platinum.—Gold is frequently alloyed with platinum, either by design or accident. The great weight of platinum and its lower value than gold,* furnish sufficient inducements for the fraudulent admixture of the two metals. Oftener, however, this alloy is the result of accident. Platinum, though wholly unalterable by fire in its pure state, is, nevertheless, capable of forming a fusible alloy with a fusible metal. The mechanical dentist's scraps are just in the condition to form this alloy, because he uses both gold and platinum, and has just enough of the more fusible metals to bring down the fusion point to the capacity of an ordinary furnace. The properties of the alloy will be described hereafter.

The two metals are easily separated from one another by the following process. The alloy is dissolved in *aqua regia*, and sal ammoniac added to the solution, which is evaporated on a water-bath nearly to dryness. Care is necessary that the heat

* The absurdly high prices, charged by furnishing-houses for chemical apparatus made from this metal, are no index of its actual commercial value, but only of the necessities and easy temper of chemists.

be not too great, and for this reason the water-bath is used. Should the temperature be raised too high, part of the chloride of gold would be dissolved, and the parting of the metals be impossible, without a new solution. The concentration having been carried so far that the yellow precipitate of platino-chloride of ammonia is just moistened by the remaining solution, alcohol is added, and the double chloride washed till the liquid comes off no longer colored. In this manner all the gold is dissolved, and the platinum remains behind, in combination with chlorine and ammonium. This double salt is ignited to obtain spongy platinum, and the alcoholic solution precipitated with protosulphate of iron, or oxalic acid, if no foreign metal be present, yields metallic gold.

Another mode, less expeditious than the former, is to fuse the alloy with silver, mill it out into thin foil, roll it up, and treat it with nitric acid, which dissolves the silver and platinum. These are to be separated as hereafter described.

Silver and Platinum.—We have already said that the alloy of these two metals is soluble in nitric acid, to which it communicates a straw yellow tint. From this solution the silver is easily precipitated by means of hydrochloric acid. The alloy may be directly acted on by sulphuric acid in the same manner already described under the head of gold. Silver dissolves in the acid, and platinum is left behind.

Copper and Platinum.—This alloy is most conveniently analyzed by dissolving it in *aqua regia*, evaporating to expel nitric acid, and precipitating platinum by means of metallic copper. Or, the copper may be dissolved out with nitric or sulphuric acid, in which the platinum of this combination is insoluble. The latter plan will not succeed when the platinum is in sufficient quantity to protect the copper, or when gold is present in large proportion.

Copper, Gold, Silver, and Platinum.—An alloy of this kind may be cupelled to get rid of the copper, and the other metals separated, as already described, or it may be dissolved in boiling *aqua regia*, which leaves the silver behind as a chloride and takes up the remaining metals. The farther process resembles the separation of gold from platinum already described. Chloride

of copper is soluble in alcohol as well as chloride of gold, and, as before, the platino-chloride of ammonium is left behind. The gold and copper are easily separated by protosulphate of iron. The choice of these methods will be regulated by the relative proportions of the metals in the alloy. If the copper is in very small quantity compared with the gold, silver, and platinum, cupellation will be advisable; if not, the latter plan should be adopted.

PLATINUM AND ITS NON-SALINE COMPOUNDS.

Platinum.—When pure, it is a soft, flexible metal, resembling silver in color, but inferior to it in brilliancy. It is very malleable, and may be hammered into leaves so thin as to be blown away by the breath. It may be drawn into wires the two-thousandth of an inch in diameter, and by coating it with silver, drawing it out, and dissolving off the investing metal, it may be reduced to a very much finer wire. A small quantity of iridium greatly diminishes its softness, malleability, and ductility; hence the necessity of separating this metal perfectly.

It is entirely unchangeable in either moist or dry air; it is not fused, tarnished, nor in any way altered by the highest heat of a smith's forge. The oxyhydrogen blowpipe and galvanism can alone break up the powerful cohesion of its particles. Dr. Hare succeeded in fusing so large a quantity as 28 ounces of it at once by means of his powerful oxyhydrogen blowpipe. This immutability of platinum at ordinary temperatures renders it an invaluable substance to the analytical chemist, who employs it for capsules, crucibles, wires for blowpipe manipulations, &c. It requires, however, caution in its use, for it is quite possible to destroy the utensils made of it, as has already been said in the preliminary chapter on metallurgic operations.

This metal was used at one time by the Russian government for the manufacture of coins. The coinage consisted of several pieces, the largest of which was the twelve-rouble piece containing 638 grains of pure Ural platinum. Now, a rouble is worth 75 cents, and its equivalents in the different precious metals are 18.5 grains of pure gold, 53.16 grains of *coined* platinum, and 277.4 grains of pure silver. Platinum, therefore, after being

worked up, is worth a little more than $\frac{1}{3}$ as much gold. The relative value of these three metals, at that time in Russia, will be better seen by a reduction of these to ounce values. An ounce of gold was worth $19.20; an ounce of platinum, after coinage, $7.02, and an ounce of pure silver, $1.30. The rapid deterioration of the metal in value, in consequence of the increased amount coined and thrown into the market, compelled the recall of this coinage.

Platinum sponge is irregular, loose, and porous in its structure, as its name imports. It is made by igniting the double chloride of platinum and ammonium, till all the volatile alkalies and the chlorine are driven off. Its density depends upon the amount of heat used to expel the volatile portions of the double salt. The higher this is, the more dense is the resulting sponge, so that when a very loose, open sponge is required, the heat must be the lowest possible ignition.

Platinum black is the most minutely divided form in which this metal is obtained. It is made by fusing platinum with copper, zinc, or potassium, and dissolving out copper with nitric acid, zinc with nitric and then with sulphuric acid, and potassium with water. Or a mixed solution of platinum and iron may be precipitated with ammonia, and ignited in an atmosphere of hydrogen. The iron being then dissolved out by hydrochloric acid, the platinum is left behind in fine powder; or, finally, this preparation may be obtained by throwing down the metal from its solutions by means of zinc or organic substances. Liebig's method is to dissolve chloride of platinum in a hot, concentrated solution of potassa, and immediately to pour alcohol upon it, constantly stirring the mixture till effervescence, showing the escape of carbonic acid, takes place. The supernatant fluid is poured off from the precipitate, which is thoroughly washed by boiling it first with alcohol, then with hydrochloric acid, then with potassa, and finally repeatedly with water. It is dried by evaporation.

These two preparations of platinum are possessed of very remarkable and energetic powers. They condense gases with great force, and sometimes with such rapidity as to drive out sufficient latent heat to ignite the metal. This property was

first discovered in the sponge, by Professor Dœbereiner, of Jena, in 1824. He found that a jet of hydrogen gas directed upon spongy platinum in the open air, gradually heated it so intensely that the metal became red, and set fire to the gas. A number of scientific toys were constructed to exhibit this experiment, and an attempt was made to make it subserve the purpose of speedy illumination, now so much more conveniently and cheaply accomplished by friction matches. Dœbereiner says that the sponge absorbs oxygen, but not nitrogen, from the air. Liebig's black is said to absorb 250 times its volume from the atmosphere. If this be true, it shows a wonderful faculty of condensation, for, estimating the pores of the black at one-fourth its entire volume, a calculation which can hardly be considered too low, the tension of the included air and its consequent condensation would be equal to a thousand atmospheres. It unites gases, forming water when placed in an atmosphere of mingled oxygen and hydrogen. Platinum wire, heated to 122°, will do the same thing. It also combines sulphurous acid and oxygen, forming sulphuric acid. It oxidates alcohol, producing acetic acid, and, if the action be sufficiently protracted, converts this into carbonic acid and water. Nor is this force confined to gases. Introduced into a solution of potassa and its nitrate in alcohol, it produces carbonic acid and ammonia. To produce these effects, it is necessary that the platinum used should have the purest possible surface, that is to say, it should have nothing on it but pure water. To attain this, potassa should be fused on the surface of the sponge, which must then be washed in pure water, dipped in oil of vitriol, and again thoroughly cleansed with water. The black may be cleansed by boiling it in sulphuric acid and washing with water and solution of ammonia.

Platinum is the heaviest of the metals. The specific gravity of the forged metal is 21.25; that of the wire 21.5. Its equivalent, according to Berzelius, is 98.68 on the hydrogen, and 1233.499 on the oxygen scale. Its symbol is Pt.

Oxide of Platinum, PtCl. 106.68.—Protoxide of platinum is obtained by digesting the protochloride in potassa water, excess of this agent being avoided, since it dissolves a portion of the oxide, forming a green solution. It is a black hydrate,

which loses its water by a gentle heat, and its oxygen by ignition. It dissolves slowly in acids, forming salts which are brown, green, red, or colorless.

It is precipitated as a brown sulphuret, by sulphuretted hydrogen, and the precipitate is redissolved by hydrosulphuret of ammonium. It forms with ammonia, by precipitation of its sulphuric acid solution, a compound which has been written $NH_3,PtO+NH_4O$. When kept for some time at a temperature of 212° F., it loses water and ammonia, and becomes NH_3Pt,O, or NH_3,PtO, which is insoluble in water or ammonia, and forms explosive salts.

Binoxide of Platinum, PtO_2. 114.68.—This oxide is precipitated as a hydrate from its solutions. Berzelius recommends that the sulphate of platinum should be exactly decomposed by nitrate of baryta. Sulphate of baryta falls, and nitrate of platinum remains in solution. The liquid is filtered, and the filtrate treated with pure soda till about half the oxide is thrown down. Should the precipitation be carried too far, a basic salt will fall. It comes down as a yellowish-brown hydrate, and, when dry, resembles iron rust. Water can be expelled at a moderate heat, but a little increase of temperature drives off oxygen, reducing it to the protoxide, and, if pushed far enough, to metal.

Its salts are formed indirectly from the bichloride and alkaline salts. They are yellow or brown, and readily let fall metallic platinum when acted on by organic substances.

Protosulphuret of platinum (PtS) is a blue-black powder, which loses sulphur by simple ignition in the air. It may be obtained by precipitating a protosalt by means of an alkaline sulphuret, or by heating the sponge or black in a covered crucible with sulphur.

Bisulphuret of platinum (PtS_2) is a blackish-gray powder, which decomposes like the last described sulphuret. It is made by precipitating the persalts with alkaline sulphurets, or by heating a mixture of 3 parts of the yellow double chloride of ammonium and platinum with 2 parts of sulphur.

Phosphuret of platinum is white, metallic, brittle, and fusible. It is formed whenever phosphorus and platinum are heated together.

Nitruret of Platinum.—The compound of protoxide of platinum and ammonia already described, when kept in a retort at 356°, gradually parts with all its hydrogen and oxygen, which pass off in the form of aqueous vapor, and a compound of three equivalents of platinum with one of nitrogen (Pt_3N) remains. When heated to 374°, nitrogen suddenly flies off, and metallic platinum remains.

ALLOYS.

Platinum readily unites with other metals when heated with them. The union is sometimes so rapid that it is attended with the evolution of heat and light. The alloys are fusible.

Potassium and sodium form with it alloys which are shining, brittle, and decomposable by water. *Antimony* makes a steel gray, brittle, crystalline alloy; and *arsenic*, a brittle and very fusible compound. Both these may be decomposed by heating them in the air; the oxidizable metal being driven off, the other remaining. The alloy with arsenic melts at a little above redness, and can be cast in moulds.

With *bismuth* and with *zinc*, its alloys are bluish-white, brittle, and fusible; with *lead*, reddish and brittle. *Tin* forms a silver white alloy with it, and so greatly increases its fusibility that it is hazardous to solder a platinum vessel with tin solder. Gold is commonly used as a solder for platinum. With *iron*, its alloy is hard and malleable, and not readily acted on by acids. One part of platinum forms with ninety-nine of iron, a compound which is not attacked by nitric acid. To *steel* it communicates toughness, and, in certain quantities, protects it from tarnish. With *copper* it forms a pale yellow, or yellowish-gray malleable alloy, which has been used in Paris for dental purposes. Von Eckart's alloy is highly elastic, a property which it does not lose by annealing. It is of the same specific gravity as silver, and not subject to tarnish. It may be hammered, rolled, polished, and drawn to the finest wire. It is composed of platinum, 2.40; silver, 3.53; copper, 11.71.

The alloy with *silver* is hard, and not subject to tarnish by sulphur.

The alloy with *gold* is of a straw yellow color, approaching white, and has a crystalline surface. It is less fusible than gold. Its behavior upon the cupel and with nitric acid has already been described in the chapter on gold. Its alloys with palladium and iridium are native, and have the same general appearances with the metal itself. The method of separating the different constituent parts of these compounds has already been described.

HALOID SALTS.

Protochloride of Platinum, PtCl.—When the deutochloride of platinum is heated to the melting point of tin, one equivalent of chlorine is given off, and this substance remains.

It is a greenish-gray powder, insoluble in water or the ox-acids, but partially soluble in hydrochloric acid. *Aqua regia* forms with it the red bichloride of platinum. The chlorides of potassium, sodium, and ammonium, combine with it to red, double salts, which have the form of KCl,PtCl. At a red heat it parts with all its chlorine.

Ammoniacal Protochlorides of Platinum.—The combinations of ammonia with chloride of platinum are so interesting, and have been used by Liebig so effectively for illustrating the laws of combination of certain compound radicals, that a somewhat minute description of them here can scarcely be considered foreign to the general purpose of this work.

Green Substance of Magnus.—This ammoniacal protochloride of platinum was first discovered by Magnus, and hence has received from Liebig the name which we give. It is made by digesting the protochloride of platinum in hot water of ammonia, which speedily converts it into a dark, grass green, insoluble, crystalline substance. Or the same substance may be formed by dissolving protochloride of platinum in boiling, moderately dilute hydrochloric acid, and pouring the solution into hot water of ammonia, or carbonate of ammonia, when green shining scales of pure ammoniacal protochloride of platinum subsides. Or sulphurous acid may be added to the bichloride of platinum, till it no longer throws down a yellow precipitate

from solution of sal ammoniac; and then excess of hot water of ammonia being added, the mixture, as it cools, lets fall the same green crystals. The principle in all these modifications of the process is the same. In all of them, protochloride of platinum is brought in contact with ammonia at a high temperature, and a combination ensues between the two bases.

The formula of this double salt is $PtCl,NH_3$. Boiled with water for some time, an isomeric yellow salt is obtained.

Yellow Salt of Reiset. Reiset's Chlorammonium-platinamid.— Reiset discovered that, when the green substance just described is digested for some time in hot caustic ammonia, a yellow solution is obtained, which, upon evaporation, yields a great quantity of yellowish-white, long, prismatic, shining crystals. These dissolve in water, and the substance may be precipitated from the aqueous solution by the addition of alcohol. The same salt may be obtained from the boiling hydrochloric solution of protochloride of platinum, by gradually adding to it carbonate of ammonia till it becomes yellow. A green substance subsides, and the solution is filtered. As it cools, the yellow $NH_3,PtCl_2$ separates, and alcohol precipitates Reiset's salt from the clear liquid above.

The formula of this salt in crystals is $PtCl,2NH_3+Aq$, or $PtNH_2+NH_4Cl+Aq$.

The behavior of these compounds is very remarkable. They have no alkaline reaction. Ammonia is not eliminated from them by either potassa or lime. Upon the green insoluble salt, hydrochloric and dilute sulphuric acids have no effect. Nitric acid dissolves it with rapid evolution of nitrous fumes, and numerous white scales crystallize out of the solution as it cools, while not a trace of ammonia can be detected in the mother liquor. A new base has now been formed by the separation of half the platinum and chlorine from the salt of Magnus and the accession of an atom of oxygen. This will be made clearer by a juxtaposition of the formulæ of the two salts:—

The green substance of Magnus is . .	$Pt_2Cl_2N_2H_6$.
The new base, which combines with the nitric acid is	$PtClN_2H_6O$.

Salts may be formed from this new base in the same manner as from a simple metallic oxide, the different acids being substituted for nitric acid.

Thus the nitrate is . . . . $PtClN_2H_6O+NO_5$.
The sulphate is . . . . $PtClN_2H_6O+SO_3$.

If a solution of the nitrate be mixed with hydrochloric acid, a heavy crystalline powder is obtained, the chloride of the compound radical.

The formula of the compound radical itself, then, is $PtClN_2H_6$.
The oxide, which forms salts with sulphuric, nitric, and other acids, is . . . . $PtClN_2H_6O$.
The chloride, obtained as just described . $PtClN_2H_6Cl$.

Gros, who discovered these salts, did not isolate the base, though its existence is most conclusively proved.

Reiset's salt is equally remarkable, for it behaves precisely like the chloride of a metal. A comparison of its behavior with that of sal ammoniac shows this most conclusively. It will be remembered that when the last-named salt is treated with sulphuric acid, its chlorine is driven off, and a sulphate of the oxide of ammonium remains. Farthermore, when a solution of sal ammoniac is mixed with a solution of bichloride of platinum, a double salt is formed.

Now, in both these cases, Reiset's compound behaves precisely like sal ammoniac. It is PtN_2H_6,Cl, and the PtN_2H_6 is the radical which corresponds to the NH_4 of the sal ammoniac. Sulphuric acid drives off chlorine and forms a sulphate of the oxide of the radical. Perchloride of platinum forms a double salt with the compound corresponding to the double chloride of platinum and ammonium, and another containing only half the quantity of bichloride of platinum.

The oxide of this base may be separated from its combinations. If to the sulphate baryta be carefully added, so as exactly to precipitate the sulphuric acid as sulphate of baryta, the pure basis is retained in solution and may be obtained in transparent colorless needles, by evaporation in the receiver of an air-pump. This basis contains the elements of protochloride

of platinum, ammonia, and water ($PtCl,2NH_3+HO$). It resembles in its behavior a caustic fixed alkali, destroying the skin, expelling ammonia from its salts, and precipitating the metallic oxides from their solutions. From a mixture of grape sugar and sulphate of copper, it throws down peroxide of copper and redissolves it when added in excess. When this mixture is heated, the peroxide is reduced to protoxide, in the same manner as when caustic potash is present.

Heated to 100°, this basis is decomposed, ammonia and water escape, and there remains a substance (PtO,NH_3) which combines with acids to form salts, and which burns in the air with evolution of ammonia, leaving metallic platinum.

When the platinum basis is brought in contact with hydrochloric acid, water is formed, and the substance originally obtained by solution of the pure protochloride of platinum in ammonia is reproduced. When the dry chlorine compound is heated to 130° or 150°, ammonia escapes, and the yellow isomeric modification of the salt of Magnus remains.

When treated with nitrate of silver, the yellow salt decomposes. Chloride of silver and two new salts, containing nitric acid and platinum, result, one of them crystallizing in yellow transparent octahedra.

If the sulphate of the oxidized platinum basis (PtN_2H_6O,SO_3) be mixed with iodide of barium, the double decomposition produces sulphate of baryta, and an iodine compound (PtN_2H_6I), corresponding to the protoxide. This protoxide is soluble in water, and decomposes on boiling into ammonia, and an iodine compound analogous to the salt of Magnus ($PtNH_3,I$).

When this iodide is treated with nitrate or sulphate of silver, iodide of silver is formed, together with the nitrate or sulphate of a new base, containing one equivalent of ammonia less ($PtNH_3O+NO_5$) ($PtNH_3O,SO_3$).

Treated with hydrochloric acid, these salts form the yellow ammoniacal protochloride of platinum; and when digested in water of ammonia, they are transformed into the nitrate or sulphate of the first series.

"According to the different notions entertained respecting the constitution of the salts, the new platinum bases may be con-

sidered as true alkalies, *i. e.* as the oxides of a compound radical formed by platinum and the elements of ammonia, and performing the part of a metal. Assuming this to be the correct view, we should have, in the first series, as the formula of

The radical	PtN_2H_6.
The oxide	PtN_2H_6O.
The chloride	PtN_2H_6Cl.
The nitrate	$PtN_2H_6O+NO_5$.
The sulphate	$PtN_2H_6O+SO_3$.

Or, if we assume the constitution of these salts to be analogous to that of the ammoniacal salts, the radical would correspond to ammonium ; the hydrogen compound, therefore, would be, in its chemical character, analogous to ammonia ; the chlorine compound would contain the elements of hydrochloric acid ; the nitrate or sulphate would contain the elements of the hydrated nitric or sulphuric acid.

"According to this view, the formula of the compound corresponding

To ammonia would be . .	PtN_2H_5.
Of that corresponding to ammonium	PtN_2H_5+H.
Of the oxide	PtN_2H_5+HO.
Of the nitrate	PtN_2H_5+HO,NO_2.
Of the sulphate	PtN_2H_5+HO,SO_3.

"According to this, the basis of the salts of Gros would differ from the basis of the last two salts, only inasmuch as it contains one equivalent of chlorine ; and, indeed, the nitrate of the non-chloruretted basis of Reiset seems, upon the addition of a solution of chlorine, to become directly transformed into the nitrate of the chloruretted basis of Gros ; at least a nitrate is obtained, by this operation, possessing the properties of the latter ; the addition of solution of iodine gives rise to the formation of a nitrate corresponding apparently to the nitrate of the ioduretted bases.

"That which is most worthy of attention in these combinations, is the circumstance that in these three bases which have been formed by the accession of platinum to the elements of ammonia, we do not observe the slightest alteration in the chemical character

of this latter substance. This fact leads us to the inference that the addition of the extraneous body, *i. e.* its accession to the elements of the ammonia, has not caused any alteration in the constitution of the latter body. And here we need only to recall to our minds the constitution of the acids and their deportment. Acids are hydrogen compounds of simple or of compound radicals, the chemical character of which, as acids, depends upon their amount of hydrogen replaceable by metals; their principal characteristic properties are independent of the number of elementary atoms contained in the atom of the radical; we see these elementary atoms increase or decrease in number without their increase or decrease exercising any influence upon the properties of the acid as an acid.

"Now we have admitted ammonia to be the hydrogen compound (hydruret) of amidogen; that is, of a radical, the chemical character of which is evidently and decidedly the very opposite to that of the radical of an acid; and we may assume that, by the accession of a compound substance, or of a new radical to the atom of ammonia, there ensues the formation of the hydrogen compound (hydruret) of a compound amide, retaining the properties of the ammonia, and this precisely because the *chemical constitution* upon which the *chemical properties* depend has remained unaltered. Of course this can only take place in cases where the chemical properties of the substance added are either analogous or similar to the chemical properties of the radical to which the substance is added, and with which it combines; for, if these properties were dissimilar or opposite, the chemical character of the radical would, of necessity, suffer some alteration; nay, under some circumstances, it might be altogether annihilated by the addition of a compound of opposite properties to those of the radical.

"Ammonia is the hydruret of amidogen; by the accession of the amide of the protochloride of platinum, or by that of the amide of platinum, the hydruret of a compound amide is formed.

$$\left.\begin{array}{l}\text{Ammonia . . . . } \mathrm{Ad+H}\\ \text{Added to this}\\ \text{Amide of protochloride of platinum } \mathrm{PtClAd}\end{array}\right\} = \mathrm{PtClAd_2+H}\left\{\begin{array}{c}\textit{Radical}\\ \textit{of the}\\ \textit{basis of Gros.}\end{array}\right.$$

Or

Ammonia . . . . Ad+H
Added to this
Amide of platinum . . . PtAd
} = $PtAd_2$+H { *Radical of the basis of Reiset.*

The basis of Reiset is PtN_2H_6O, or PtN_2H_5+HO.
The chlorine compound is PtN_2H_6Cl, or PtN_2H_5+HCl.

"In this chlorine compound we may assume chlorine to exist as an ultimate constituent in the form of hydrochloric acid. It is farther possible that, as Reiset is inclined to think, the accession of a metallic oxide—of protoxide of platinum, for instance—to the elements of ammonia, imparts to the latter the properties of a base, just in the same manner as the accession of protoxide of hydrogen (water) does. In this case, the metal of the metallic oxide would perform exactly the same part as the hydrogen does.

Basis in the ammoniacal salts { NH_3, HO } = { NH_3, PtO } Basis in the platinum salts of the second series.

Basis in cuprum sulphurico-ammoniatum { $2NH_3$, HO } = { $2NH_3$, PtO } Platinum basis of the salts of Reiset.

"Upon looking at the chlorine compound of the basis of Gros, we farther find that this compound contains the elements of perchloride of platinum and of ammonia:—

Chlorine compound of Gros, $PtClN_2H_6Cl$, or $PtClN_2H_5$+Cl.
Ammoniated perchloride of platinum, $PtCl_2+N_2H_6$.

"Now we find, in fact, that perchloride of platinum, when thrown into a warm solution of ammonia, dissolves therein to a large amount, forming a nearly colorless fluid, which, upon the addition of alcohol, yields a copious, white, flocculent precipitate. By treating this precipitate with nitric acid, a crystallizable and soluble white salt is obtained, very similar to, or—what is highly probable—identical with the nitrate of the basis of Gros. The precipitate itself, however, shows by no means the properties of the chlorine compound of the basis of Gros; for this latter is yellow, and of very difficult solubility in water, whilst the ammoniacal perchloride of platinum is partially redecomposed upon evaporation, and of exceedingly easy solubility in water."*

* Liebig, Lectures on Organic Chemistry.

If it be thought that too much space has been expended upon the history of these remarkable reactions, the author's only apology must be made in the words of the great chemist from whom he has so largely quoted: "I have entered upon this discussion of the properties and deportment of these remarkable bases principally because it will tend to elucidate the nature of a great and important class of compounds, which, as true organic bases, do not comport themselves like the metallic oxides, but like ammonia; the saturating capacity of which does not depend, as is the case with the metallic oxides, upon their amount of oxygen, but upon a certain and definite amount of hydrogen in the acid which is added to their elements."

Bichloride of Platinum, $PtCl_2$.—This chloride is obtained by dissolving platinum in nitro-hydrochloric acid, and evaporating to dryness at a very gentle heat, when it remains as a red hydrate, becoming brown after the expulsion of its water. Should the heat be too high, the salt is partially decomposed, protochloride of platinum being formed, which gives it a darker color. The best mode of regulating the heat is to use a water-bath. It crystallizes with ten equivalents of water.

When free from palladium and iridium, and from protochloride of platinum, its solution is yellow, with a reddish cast. It is very soluble and highly deliquescent. Its ethereal solution gradually deposits metallic platinum. Heat reduces it first to protochloride and then to metal.

The bichloride of platinum forms double salts with many metallic chlorides. The double chloride of *sodium* and *platinum*, $NaCl,PtCl_2+6HO$, is crystallizable and soluble both in water and alcohol. The *potassium* salt ($KCl,PtCl_2$) is lemon yellow, scarcely soluble in cold water, a little more soluble in hot water, insoluble in alcohol of 60 per cent. At a full red heat it is decomposed, chlorine being driven off, and metallic platinum and chloride of potassium being left behind. The *ammonium* salt ($NH_4Cl,PtCl_2$) has the same degree of solubility as the potassium salt, but it is more easily decomposed by heat, leaving nothing but spongy platinum.

Protiodide of Platinum, PtI.—This compound is prepared by digesting the protochloride of platinum with iodide of potas-

sium. It is a black powder, insoluble in water and alcohol, and unchangeable by the acids. With ammonia, it forms the ammoniacal iodide already described. At a high heat, iodine is driven off.

Biniodide of Platinum, PtI_2.—When iodide of potassium is mixed with perchloride of platinum in dilute solution, the liquid changes first to orange red, and then to claret color, without precipitation; but when the solution is boiled, a black, sometimes crystalline precipitate subsides, which should be washed with hot water, and dried at a temperature not exceeding 212°. It is tasteless and inodorous, insoluble in water at any temperature. It is sparingly soluble in alcohol. Acids act feebly on it, but it is decomposed by alkali, and begins to lose iodine at 270°.

The *bromides* resemble the iodides both in preparation and general properties.

OXYSALTS.

Sulphate of Protoxide of Platinum, PtO,SO_3.—This salt is obtained by dissolving the recently precipitated oxide of platinum in sulphuric acid. Like the nitrate, it forms a brown solution. The combination with ammonia, made by precipitating the ammoniacal chloride by nitrate of silver, has been already alluded to.

Sulphate of binoxide of platinum (PtO_2,SO_3) is obtained by decomposing the bichloride by means of sulphuric acid. It is soluble and crystallizable.

Sulphite of protoxide of platinum (PtO,SO_2) is made by suspending the oxide in water, and passing a stream of sulphurous acid gas through the mixture. It forms double salts with soda and ammonia. There is also a sulphite of the binoxide.

Nitrate of the binoxide of platinum is obtained by direct action, or by double decomposition of the sulphate with nitrate of baryta. It forms basic double salts with potassa and soda.

CHAPTER X.

MERCURY.

THE fact that an amalgam of mercury with other metals has been used, and is still recommended in some quarters as a filling for teeth, renders it necessary that a brief description of this metal should be subjoined to our account of the metals used by the dentist.

Mercury is found native, disseminated through the vein-stone, in mines of this metal. Sometimes it collects in such abundance in hollows in the rock that it may be readily dipped out. More commonly it is found as a sulphuret, the *native cinnabar*. This is occasionally found crystallized in rhombohedral prisms of an adamantine lustre, and a color varying from cochineal red to a reddish lead gray. The amorphous variety, of a dull red color, is more frequently met with.

The principal mines of this metal are those of Idria, in Austria; of Almaden, in Spain; of Drei-Königszug, in the Palatinate; and of Guancavelica, in Peru. There are also mines in Hungary and Bohemia, the joint product of which is rated at 30 or 40 tons a year. Mexico, Sweden, China, Japan, and Chili, also contain mines of this metal.

The oldest of all the mines is that of Almaden, in Spain. The Greeks imported cinnabar from them; and Rome, in Pliny's time, received annually 100,000 pounds of the metal from the same source. According to Dr. Ure, these mines employ a force of 700 miners and 200 smelters, and have produced, since 1827, 200,000 cwt. of mercury a year. Some idea may be formed of their immense value from the fact that, though actively worked for so many centuries, the mines are not yet 1,000 feet below the surface. The vein now worked is from 14 to 16 yards thick, and is still thicker at the crossings. Owing to the barbarous method of working, much mercury is lost, only 10 per

cent. being obtained from the ore. The geological formation is an argillaceous schist and sandstone grit, deposited in horizontal beds, intersected occasionally by eruptions of granite and black porphyry.

The mines of Idria, discovered in 1497, are mined at the depth of 280 yards for the bituminous sulphuret. Dr. Ure says it would be easy to procure 600 tons a year from these mines; but the Austrian government, in order to keep up the price of quicksilver, has limited its production to one-fourth of that sum. In 1803, a destructive fire broke out in these mines, and was only extinguished by inundating all the subterraneous workings. More than 900 persons in the neighborhood of the mines suffered from nervous tremblings and other diseases, generated by the large quantity of mercury sublimed by the heat.

The mines of the Palatinate are numerous, and occur in various geological formations. Those of Drei-Königszug are the most important. They are worked at a depth of more than 220 yards, the ore being a sandstone strongly impregnated with cinnabar. The annual yield of these mines is about 30 tons.

The mines of Guancavelica yielded, from 1570, at which time they were first opened, up to 1800, 53,700 tons of metal. According to Ure, at the beginning of this century, the annual produce was from 170 to 180 tons. The mercury is used up in the country for amalgamating gold and silver.

METALLURGIC TREATMENT OF MERCURIAL ORES.

The reduction of mercury from its ores is a genuine dry distillation, which is conducted in different modes at different mines. A very rude process is adopted in South America and in China. Wells or pits are heated with a brushwood fire, and the ores are thrown in. As they cool, the quicksilver is condensed and collected from the cavities in which it has been deposited.

At Idria, a very extensive series of chambers communicates with a large roasting kiln, which is divided into apartments by three arches. The ores are classified before being introduced. The larger and richer bits are placed upon the lower arch. The

second class, which consists of the smaller pieces of ore, is put upon the second arch; and the third class, consisting of fine sand and *schlich*, upon the highest arch. The strong oxidating flame, which plays over these ores, converts the sulphur into sulphurous acid, which escapes, while the liberated mercury is volatilized and gradually condensed in the chambers.

Forty men are occupied three hours in charging this furnace, which is kept, during the ten or twelve hours the distillation lasts, at a cherry red heat. The fuel employed is beech-wood. A complete charge is from 1,000 to 1,200 quintals of ore, which yield from 80 to 90 quintals of metallic mercury. The furnace requires five or six days to cool, so that but one charge can be worked in a week. The furnace is 180 feet long, and 30 feet high.

The *aludel* furnace is used in Spain. It consists of a furnace with one arch and two chimneys. One of these is at the same end with the fireplace, and carries off the greater portion of the smoke. The other is at the farther end, at which the *aludels* terminate, and serves to carry off the remaining smoke. The aludels are pipes, made by fitting into one another a long series of earthen adopters. These are arranged upon a double inclined plane, and terminate in a chamber, which communicates with the second chimney just spoken of. The ores are placed upon the arch and the fire kindled. As the heat is raised, the mercury and the gases distil over and pass through the aludels. The greater portion of the metal runs into a gutter provided for its escape. Part remains in the *aludels*, and part comes over with the smoke and uncondensed gases. This is deposited in an iron vessel at the bottom of the chamber, while the smoke and gas pass out at the second chimney.

The *gallery* of the Palatinate is an elongated furnace, in which are arranged rows of earthen retorts called *cucurbits*. Each of these communicates with a separate receiver, which is partly filled with water. The number for each gallery varies from 30 to 52. Each cucurbit is charged with from 56 to 70 pounds of cinnabar, mixed with from 15 to 18 of quicklime. The sulphuret of mercury is decomposed by the lime, forming sulphuret

of calcium and sulphate of lime, and setting free metallic mercury, which distils over.

Dr. Ure erected at Landsberg, in 1847, an apparatus which was a great improvement on the old methods of distilling mercury. It consists of a series of retorts like those employed in the manufacture of coal gas. They are set in masonry, and each of them is fitted at one end with eduction-pipe, and, at the other, with an air-tight stopper, closed by an iron screw. Connected with the pipes is a large condenser, containing water, and set in a wooden trough, also filled with that fluid. They are kept constantly in a uniform state of ignition. Each retort will contain five hundred weight of ore, from which the metal is almost entirely expelled in the course of three hours.

MERCURY AND ITS NON-SALINE COMPOUNDS.

Mercury.—This is easily distinguished from all other metals by its liquidity at ordinary temperatures. It is silver white, with a strong metallic lustre, which it does not lose when exposed to the air. At 39° it is solid, and is then both ductile and malleable. In polar latitudes, mercury often freezes, and the same result may be attained in the laboratory by using a freezing mixture composed of ether and solid carbonic acid, or of pounded ice and crystallized chloride of calcium. It may be obtained in brilliant octahedral crystals, by slowly congealing a quantity of it in a platinum crucible, arresting the process before the solidification is complete, and pouring off the liquid portion.

It expands with great regularity by equal increments of heat, until near its boiling point, 680°. It volatilizes far below its boiling point, at the ordinary temperatures of the atmosphere, and even as low as 32°. This may be proved by suspending a sheet of gold leaf in the upper part of a bottle containing mercury. In a few days that portion of the gold nearest the mercury will be whitened, while that at the upper portion of the bottle will be unaffected, since the vapor of mercury forms a very shallow stratum just above the surface of the metallic bath.

The mercury of commerce, when obtained directly from the

mines, is usually contaminated only with a little oxide. After it has passed through two or three hands, however, it becomes abominably filthy, being adulterated with a variety of cheap metals. In consequence of this contamination, it tarnishes rapidly, a gray film of oxide floating upon the surface.

It is purified by repeated distillation, but is hardly ever obtained absolutely pure by this process alone, some of the impurities invariably passing over into the receiver. To remove these, the mercury is treated with common nitric acid, diluted with about twice its volume of distilled water. The whole is then heated to about 110° F., and nitrate of suboxide of mercury will be rapidly formed. This nitrate and the free acid react on the foreign metals present, which are held in solution in the form of salts. Any oxide of mercury originally present is dissolved by the nitric acid. This action is to be continued for twenty-four hours, the mixture being repeatedly agitated. The water is now evaporated, and the nitrate, which remains as a crystalline crust on the surface of the mercury, skimmed off. The metallic mercury is washed with distilled water, and dried under a bell-glass, over a saucer of caustic lime.

Strong hydrochloric acid does not affect mercury, even though boiled upon it. Dilute sulphuric acid fails to dissolve it, but the concentrated acid, aided by heat, attacks it violently. Nitric acid acts very energetically upon it, even in the cold, and, when moderately diluted with water, binoxide of nitrogen is plentifully evolved.

The specific gravity of mercury at 78.8° is 13.530; at 47°, 13.545; while that of frozen mercury is 15.612. The specific gravity of its vapor is 6.976. Its symbol is Hg. Its atomic weight has been recently changed, and with it the nomenclature of its compounds. According to Berzelius, it is 1265.828 on the oxygen, and 101.266 on the hydrogen scale. Swanberg makes it 1250.9 on the former, and 100.07 on the latter.

Oxides. *Suboxide of Mercury*, Hg_2O.—This, which was formerly called the protoxide, is a brownish-black powder, decomposing by light and warmth into oxygen and the metal, and giving up its oxygen to deoxidating agents generally. It

is obtained by treating one of its salts or the subchloride with caustic alkali, washing and drying.

It is a feeble base. The soluble salts are colorless; the basic salts yellow, and generally soluble. Caustic alkalies give with these salts a black precipitate; iodide of potassium, a yellow olive green; chromate of potassa, a deep crimson; and sulphuretted hydrogen, a black precipitate.

Oxide of Mercury, HgO.—This oxide, known as red oxide, red precipitate, or deutoxide, is formed by decomposing the nitrate through the agency of heat. It is a red crystalline and shining, or amorphous and dull powder, decomposed in the same manner as the suboxide. Heated with sulphur, it explodes.

Its salts are colorless; yellow, if basic; acid in their reaction; styptic in their taste, and poisonous in their quality. Caustic alkali throws down an orange red; carbonates, a brownish-red; ammonia, a white; solution of galls, a yellow; chromate of potassa, an orange red; iodide of potassium, a brilliant red; sulphuretted hydrogen, a black, a white, or a red precipitate, according to the quantity of the reagent.

Sulphurets. *Subsulphuret of Mercury*, Hg_2S.—This sulphuret is prepared by passing a stream of sulphuretted hydrogen through a solution of nitrate of the suboxide. It is a black powder, which is oxidized by digestion in strong nitric acid. Heat resolves it into sulphuret and metallic mercury.

Sulphuret of Mercury, HgS.—This substance occurs native as cinnabar. It is also prepared artificially, and constitutes the beautiful pigment, vermilion. It is made by fusing sulphur and mercury together, and volatilizing the resulting cinnabar, or by treating *Ethiops mineral* with a warm solution of potassa.

Ethiops mineral was supposed by Brande to be a mixture of sulphur and the sulphuret. It is made by rubbing mercury and sulphur together.

Phosphuret of mercury, HgP, is black, when formed by digesting mercury and phosphorus with water; orange yellow, when made by passing phosphuretted hydrogen over the dry chloride.

Nitruret of mercury, NHg_3, is a dark brown, highly explosive powder, made by heating the red oxide saturated with ammonia.

AMALGAMS.

The alloys of mercury with other metals have received the name of amalgams. They are made by mixing the metals together in the cold, either alone or with some compound which favors their union. The fluid amalgams are solutions of the genuine amalgams in excess of mercury. The more solid amalgams are crystalline, and so soft as to be capable of being kneaded.

Of the numerous amalgams which have been made, but a few are in general use. That employed for the electrical machine is composed of mercury 50, tin 25, zinc 25. The silvering for mirrors is a mixture of mercury 30, tin 70. Glass globes are silvered with a compound of mercury 80, bismuth 20. Gilders' amalgam contains 10 parts of gold to 90 of mercury, while that for silvering is composed of 15 parts of silver to 85 of gold.

Amalgams of mercury with silver, gold, and other metals, have been used for the purpose of filling teeth. The deleterious effects of such fillings will be presently examined.* One of the vilest combinations of this class is that made by mixing together 9 parts of mercury, 17 of tin, 45.5 of bismuth, and 28.5 of lead.

HALOID SALTS.

Subchloride of Mercury, Hg_2Cl.—This is the compound long known as *calomel*. It has also been called protochloride, dichloride, mild chloride, and submuriate. It is prepared by intimately mixing 4 parts of the chloride with 3 of metallic mercury, subliming and washing thoroughly to free it from corrosive sublimate. It occurs native as *horn quicksilver*.

It is insoluble in water; decomposed by contact with many of the metals, by heating with sulphur and some sulphurets, or with sulphuric, nitric, or muriatic acid, by subliming it with sal ammoniac; in all which cases the chloride is formed. Treated with a solution of potassa or soda, it yields the suboxide, and

* See Effects of Mercury on the System.

under caustic ammonia it forms a black subchloramide of mercury. Chloride of sodium assists its solution, and as this alkaline salt is always found in the stomach, we are no longer under the necessity of supposing calomel to undergo a gradual metamorphosis into corrosive sublimate previous to absorption.

Chloride of Mercury, HgCl.—This intensely corrosive poison is formed by crystallization from a solution of the red oxide or of calomel in hydrochloric acid. It crystallizes in opaque rhombic prisms.

At 563° it fuses and volatilizes, the specific gravity of its vapor being 9420. Exposed to the rays of the sun, its solution is decomposed, oxygen escapes, hydrochloric acid is formed, and subchloride of mercury precipitated. It is decomposed by several metals, by sulphur, phosphorus, and their lower acids. Potash throws down from its solution a brown oxychloride of mercury.

Vegetable and animal albumen form with it a white insoluble precipitate, a compound of calomel and albumen. Consequently, albumen, in one form or another, commonly as white of egg, has been recommended and largely used as an antidote to this poison. Mialhe prefers the moist, recently precipitated sulphuret of iron, which immediately decomposes the chloride of mercury.

The chloride of mercury enters into combination with a great variety of substances, forming many double salts, which do not require special examination in this place.

Bromides.—Bromine, like chlorine, forms with mercury two salts, one insoluble, analogous to calomel, the other soluble, like corrosive sublimate.

Iodides.—The *subiodide* is a greenish-yellow powder, easily decomposed by light, made by mixing 200 parts of mercury with 126 parts of iodine moistened with alcohol, and extracting the excess of iodine with alcohol.

The *iodide* is a fine red powder, obtained by precipitating a salt of the red oxide by an alkaline iodide. It sublimes in brilliant red quadratic, or in yellow right rhombic crystals.

The *fluoride* is an orange yellow powder.

OXYSALTS.

A. *Salts of Black Oxide. Subsulphate of Mercury*, Hg_2OSO_3. —This is obtained by heating mercury with oil of vitriol, till all the metal disappears and a white powder takes its place. This is dissolved in boiling water, from which it crystallizes.

Nitrate of the Suboxide of Mercury. Protonitrate of Mercury, Hg_2ONO_5+2HO.—This salt crystallizes from a solution of mercury in excess of cold nitric acid. Water decomposes it into a basic salt. When kept in a laboratory as a chemical reagent, it must always have some metallic mercury in the bottom of the bottle.

The *phosphate* is a white crystalline powder, insoluble in phosphoric acid and decomposed by heat. It is formed by double decomposition.

B. *Salts of Red Oxide. Sulphate of Oxide of Mercury*, $HgOSO_3$.—When 5 parts of sulphuric acid are heated with 4 of mercury, a dry crystalline mass, the sulphate of the red oxide, is formed. Water decomposes it into a soluble salt and a yellow, nearly insoluble, basic salt, the *turpeth mineral* of the older chemists. A number of compound salts are formed from this sulphate.

Nitrate of Oxide of Mercury.—The neutral salt is known only in solution, from which a basic salt crystallizes. By treating the crystals with water warmed to different temperatures, two basic salts, one yellow and the other brown, are formed. This salt also forms numerous double salts with ammonia, and with other substances.

The *phosphate* is white, insoluble in water, but soluble in phosphoric acid and ammoniacal salts. The *carbonate* is a pale red, insoluble powder.

The other salts do not demand special attention here.

EFFECTS OF MERCURY ON THE SYSTEM.

The general influence of mercury upon the system is so well known, that we need not do more than glance at its more prominent features.

The ordinary alterative action of this metal when administered in properly regulated doses, is attended by no especial disturbance of the system. But at times it does not operate upon the economy with such tranquillity. A febrile condition, or at least a state approximating fever, is not uncommon. At such times the surface becomes warm, the circulation is accelerated, the pulse is frequent and jerking, the face is slightly flushed, the nervous impressibility is heightened; in short, there is a general excitement of all the functions. The glandular system is especially acted on; the liver secretes more bile, the salivary glands eliminate more saliva; and in this, as well as in the green discharges from the bowels, the metal may be detected.

When mercury is about to spend its force upon the glands of the mouth, the earliest indication of its action is an unpleasant metallic taste like that of copper or brass. Presently, the gums become sore and tender, the mucous membrane is inflamed, the teeth suffer with disagreeable sensations, which are referred to the fangs, and these are raised to actual pain when the jaws are firmly closed. Presently, the gums swell and become spongy, then a whitish line is seen along the edge of the teeth, and the peculiar mercurial fetor is developed. The salivary glands are swollen and hot, the jaws stiff and painful. After this condition of things has lasted a short time, a copious flow of saliva takes place. The disease does not always stop here. The cheek is puffed out with a red swelling, which gradually becomes more and more livid, till a gangrene sets in which sweeps it away, slough after slough laying bare the cavity of the mouth, and hurrying the unhappy sufferer to the grave. Sometimes the ulcerations attack the gums, break them down, seize upon the periosteum, penetrate the bone, which becomes carious and spongy, and finally exfoliates, leaving the most hideous gaps in the face. At other times, this ulceration or gangrene extends among the soft parts, and opens the bloodvessels, giving rise to the most destructive hemorrhage.

Nor is its influence by any means confined to the cavity of the mouth. With or without salivation, it exerts the most baneful influence over the economy. At times, it acts as a powerful and dangerous sedative to the circulation. The countenance

becomes pale and anxious, the pulse small and frequent. There is much anxiety about the præcordia, great nervous agitation, and extreme and alarming prostration of strength.

At other times, an eruption breaks out over the surface, which has been called *hydrargyria*, *eczema mercuriale*, and *lepra mercurialis*.

The most distressing effects it produces, however, are the affections of the nervous system. These are especially experienced by those who contract the poison by slow and gradual absorption of the metal. One of the most frequent of these disorders is a form of *paralysis agitans*. The tremors of the limbs are so considerable that the patient is unable to walk without staggering, or to hold anything in his hand. He stammers, and finds it extremely difficult to speak at all. His memory fails him, his intellect becomes weak, and his sight is dimmed. Such phenomena as these are constantly met with among gilders, looking-glass makers, and workmen in quicksilver mines.

So virulent a poison as this should never, except in cases of the sternest necessity, be introduced into the system, and then it should be done with the greatest care, and so managed that its absorption may be controlled, or that the quantity to be taken in may be regulated.

How are these conditions fulfilled when an amalgam is introduced into a tooth? Not at all. The secretions of the mouth float around the metal, and act upon it. An important part is also played by the other constituents of the filling, which, together with the mercury, form a galvanic apparatus, greatly accelerating the solution of this metal.

The *amalgam question*, as it has been called, is thus answered with the utmost promptitude by chemistry. To the chemist, it has but one side; it needs but to be stated to be immediately decided upon. The use of a mercurial amalgam is, under all circumstances, wrong; for the simple reason that we have no guarantee that the most frightful results of mercurial poisoning will not take place. The introduction of lead into it, as in the villanous compound, of which a formula has been given, is a step farther into the wrong.

That the metal itself, as well as its salts, is capable of pro-

ducing these symptoms, is a matter of such commonplace notoriety that the veriest tyro is familiar with it. That a soluble compound is formed in the mouth, which can be absorbed by the teeth, is proved by simple inspection of a tooth which has been filled with it. I have seen the metallic discoloration extending into the fang.

The dose of mercury which produces its peculiar effects is well known to be extremely variable. The probability is that, except in rare cases, but a small portion of it ever gets access at any one time into the economy. The effect experienced is not that of the last dose, however large, but of all that has effected a lodgement in the tissues. The recent observations of Melsens and Budd have shown that both mercury and lead, even in the form of insoluble salts, may remain a long while combined, as it were, with the tissues, producing varied phenomena of disease, and then may be set free by iodide of potassium, so as to enter the blood and produce their specific primary effects upon the organism. Now, if these insoluble compounds are capable of producing so much mischief, by what possible process of reasoning can any one arrive at the conclusion that metallic mercury, which we all know to be soluble in the fluids, will prove inert? If it be urged that the smallness of the quantity and the gradual nature of the absorption is a guarantee against poisoning, a reply is to be found in the well-known fact that small portions of metallic mercury, daily absorbed, produce the most distressing and unmanageable forms of mercurial poisoning. It is precisely in this manner that the workmen in mercury introduce the metal into their systems.*

* As an example of the remarkably small quantity of a metal which is sometimes sufficient to poison, a case recently reported to the American Medical Association, and copied in nearly all the journals, may be cited. The most obstinate and protracted symptoms of lead poisoning occurred in a gentleman who had been in the habit of *chewing metallic lead.*

PART II.

THE MATERIALS USED IN MAKING INCORRUPTIBLE TEETH.

CHAPTER I.

SILICON.

THE basis of all glass or porcelain is silicic acid, which is itself an oxide of an elementary body, *silicon*. Davy was the first to demonstrate this, by bringing the vapor of potassium in contact with pure silicic acid heated to whiteness. Silicate of potassa was formed, and silicon was found diffused through it in the form of black particles like plumbago. It was then taken for a metal and called *silicium*. Thomson, however, regarded it as a metalloid, and classified it with carbon and boron; and this opinion has received the sanction of the great name of Berzelius. The latter chemist first obtained this substance pure in 1824.

The Swedish philosopher procured it by the action of potassium on fluosilicic acid gas. It is more conveniently obtained, however, from the double fluoride of silicon and potassium, or sodium previously dried at a temperature approaching that of redness. Ten parts of silicofluoride of potassium are mixed with from 8 to 9 of potassium in an iron or glass tube, and the potassium fused and stirred with the salt. It is then heated with a spirit-lamp; the temperature becomes suddenly raised to ignition by the energetic action of the potassium on the silica, the base of which is alloyed, as it were, with the potassium.

On throwing the brown mixture into water, silicon separates, and fluoride of potassium and potassa are left in solution. It is washed thoroughly, first in cold and then in hot water, till everything soluble is taken up.

Another mode of obtaining it is to expose the chloride of silicon to heat in a tube, so arranged that the vapor of this substance shall pass over potassium, air having first been expelled from the apparatus. The excess of the chloride having been driven off, after the union of the potassium with the chlorine, the whole is put into water, and, chloride of potassium having been dissolved out, silicon remains.

As thus procured, silicon is a dark nut-brown powder, which does not stain the fingers. It is a non-conductor of electricity. It exists in two distinct forms, like its oxide, which also has two modifications.

The first of these is insoluble in any of the strong acids except the hydrofluoric. It is soluble in caustic potassa. It burns readily and vividly in the air, and more vividly in oxygen gas. The result of this combustion is a coating of silicic acid, which protects the centre from the farther action of the air.

This inner portion is found, on removing the superficial coat, to be completely changed in its properties. It is now no longer combustible, even in oxygen gas. It is darker and denser than before, so that it sinks in oil of vitriol. It resists the action of hydrofluoric acid and potassa, and is unaltered when ignited with nitrate of potassa. It is soluble, however, in nitro-hydrofluoric acid.

The symbol of silicon is Si; its combining number, according to Berzelius, 22.185 on the hydrogen, and 227.312 on the oxygen scale.

Silicic Acid, SiO_3. 30.155.—Silica, or silicic acid, is abundantly diffused throughout nature. It forms the chief portion of most of the simple minerals, and gives lustre and hardness to the greater number of gems. These are, indeed, nothing but salts of this widely distributed acid. In quartz, rock crystal, chalcedony, feldspar, sandstone, and other bulky rocks, it is the principal ingredient. It may be obtained of sufficient purity for ordinary purposes by igniting transparent rock-crystal,

quenching it in water when fully incandescent, and reducing the crumbling mass to powder.

To obtain it perfectly pure, it is necessary to fuse quartz, feldspar, or some of the silicious minerals with four times its weight of carbonate of soda or potassa, or a mixture of both. The resulting glassy mass is then dissolved in pure hydrochloric acid, evaporated to dryness, digested in hydrochloric acid, and then thoroughly washed, first with dilute hydrochloric acid, afterwards with water.

Silicic acid exists in two distinct modifications. The first variety is largely soluble in water, and is obtained by dissolving a soluble silicate in hydrochloric acid, or by oxidating the sulphuret of silicon in water. It then appears as a bulky, gelatinous hydrate, converting a large quantity of fluid into a tremulous jelly, soluble both in water and acid, and partially decomposed by simple drying, but losing all its water only after ignition.

Evaporation to dryness converts this hydrate into the second modification. This is totally insoluble in water or acids. It is a white gritty powder, communicating a rough and dry sensation to the fingers when rubbed between them. It is insipid and inodorous. It is infusible at the highest heat of a furnace, but melts readily to a clear glass, which may be drawn out in threads, before the oxyhydrogen blowpipe. When this fused silica is dropped into water, it becomes so very hard as to indent a steel pestle and mortar. It is volatile in the vapor of water, for steam passed through tubes containing silica heated to whiteness deposits, on cooling, large quantities of it as a snow-white powder.

At common temperatures, it is a feeble acid, but, at a high heat, it expels most acids from their salts. With the fixed alkalies, it forms substances which vary with the relative proportions of the ingredients used. These are obtained by fusing silica with the carbonate of the alkali. Violent ebullition takes place in consequence of the rapid escape of carbonic acid gas, and a vitreous substance results, which is rather soluble, if the alkali has been to the silica as three to one. The solution which was formerly called *liquor silicum*, has an alkaline reaction, and

absorbs carbonic acid from the atmosphere, becoming partially decomposed. Concentrated acids precipitate the silica as the gelatinous hydrate already described. Reversing the proportions of the ingredients, we obtain the well-known hard, insoluble silicate, glass.

Sulphuret of Silicon, SiS_3.—This substance, which is obtained by heating silicon in the vapor of sulphur, is white, earthy, decomposed by moist air or water, with the formation of sulphuretted hydrogen and the soluble modification of silicic acid.

Chloride of Silicon, $SiCl_3$.—When a stiff paste, made of finely powdered silica, oil, and charcoal, is first charred in a close crucible, and then pulverized and ignited in a porcelain tube while a stream of chlorine gas passes over it, a new substance is formed, which may be condensed in a cooled receiver. It is the chloride of silicon, a very volatile liquid, boiling at 122°, with a very pungent acid odor, fuming in the air, and decomposing in water into hydrochloric and silicic acids.

Bromide of Silicon, $SiBr_3$, is made like the former, substituting bromine for chlorine. It is a fuming, colorless liquid, boiling at about 300°, and freezing at from 5° to 10°.

Hydrofluosilicic Acid, $2SiF_3,HF$.—When equal parts of finely powdered fluor spar and sand or pounded glass are heated in a retort with six parts of sulphuric acid, a gas, fluosilicic acid, is formed, which may be collected in perfectly dry vessels over mercury. Should this gas be transmitted through water, the liquid becomes gelatinous in consequence of the deposition of silica; and, on being filtered from the silicic acid, a clear solution of hydrofluosilicic acid is obtained.

This acid is a useful reagent in the laboratory, serving, among other purposes, to separate baryta from strontia.

CHAPTER II.

ALUMINUM.

Alumina is also a very abundant substance in nature, and is, like silica, an oxide. Davy first demonstrated this by passing the vapor of potassium over alumina heated to whiteness, thus deoxidating the earth and procuring metallic aluminum.

Wöhler obtained it in sufficient quantity to examine its properties by mixing chloride of aluminum with potassium in a platinum crucible, and heating it over a spirit-lamp. The action is so violent that sudden ignition takes place, and the crucible becomes redhot. The substances are generally found to have been completely fused. After the crucible has thoroughly cooled, the gray fused mass is well washed in water, the chloride of potassium being taken up, and gray metallic aluminum in powder and spangles remaining. Liebig obtained aluminum by introducing the chloride into a closed bent tube, and placing near it, in the horizontal limb, some fragments of metallic potassium, so that when the chloride is heated, its vapor shall pass over the metal. The same action takes place as in the last-named process, and the chloride of potassium is removed from the aluminum in the same way.

It is a gray powder, resembling platinum, containing scales or spangles of a metallic lustre, and a few small spongy masses, white and bright, like metallic tin. For fusion, it requires a temperature higher than that at which cast-iron is liquefied. By this means, or by strong pressure, the powder just described is condensed, and possesses a strong and decided metallic lustre. In its finely divided state, it does not conduct electricity, though when fused or pressed, it behaves towards this imponderable like other metals.

Heated to redness in the air, it burns with a vivid light, and is oxidated to alumina. Sprinkled in the flame of a candle,

brilliant sparks are given off like those emitted by iron when burnt in oxygen gas. Heated to redness in pure oxygen, it burns with a vivid light and intense heat. The resulting alumina is partially vitrified, of a yellowish color, and hard enough to cut glass. It is, in fact, an artificial corundum. Heated nearly to redness in an atmosphere of chlorine, it takes fire, and chloride of aluminum is sublimed.

Aluminum is not oxidated by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. When the water is heated to the boiling point, a little hydrogen gas escapes, and the metal is slowly oxidated; though even after protracted ebullition, the smallest particles suffer scarcely any change.

The symbol of aluminum is Al; its atomic weight 13.72 on the hydrogen, and 171.17 on the oxygen scale. This is calculated from the chemical analogy of alumina with sesquioxide of iron, so that it too is rated as a sesquioxide.

Sesquioxide of Alumina, Al_2O_3. *Alumina.*—This oxide is found everywhere over the surface of the earth. Feldspar, the slates, the clays, and many other of the great mountain and alluvial masses, consist to a great extent of this earth. It is found pure and crystallized in *corundum*, the varieties of which are adamantine spar, topaz, ruby, sapphire, &c. It is extremely hard, transparent, and lustrous.

Artificially, it is obtained by a variety of methods. The easiest of these is to ignite pure ammoniacal alum, when the volatile alkali and the sulphuric acid are driven off, leaving the pure alumina. Berzelius obtained it by precipitating a solution of alum with an excess of carbonate of soda or of potassa, and digesting the precipitate for some time in the precipitant; washing it well, dissolving it in hydrochloric acid, filtering, precipitating with ammonia, and igniting. Liebig throws down the sulphuric acid from alum by chloride of barium. Chlorides of potassium, aluminum, and barium remain in solution. He filters, and evaporates to dryness, ignites the remainder, and washes out the chlorides with water.

As thus obtained, it is a white, loose, soft, inodorous, and insipid powder. After strong ignition, it contracts, and be-

comes sufficiently hard to strike fire with steel. It is infusible at the highest furnace heats, but melts before the oxyhydrogen jet more easily than silica. Gaudin fused it to a bead the size of a hazelnut, which contained in its cavity crystals of corundum. It has a powerful affinity for water, attracting it from the air, and forming with it a paste which is quite plastic, and can be wrought into a variety of forms. When once moistened, it will not part with its water at a heat short of whiteness. It contracts or shrinks in proportion as water is expelled. Upon this property is founded the old pyrometer of Wedgewood.

It has a double set of affinities, so that it appears alternately to act the part of an acid and an alkali. It forms salts on the one hand with the acids, and on the other, combines with the alkalies. Potassa readily dissolves it, so do the acids, even the acetic. It changes its character, however, after ignition, when it becomes extremely difficult to dissolve it.

It is the basis of all porcelain and pottery wares as well as of brick. Its affinity for colors also renders it a most useful agent to the dyer in fixing his tints upon vegetable fibre.

Aluminum combines with sulphur, phosphorus, tellurium, &c. but these compounds possess so little general interest that we shall pass them by without description.

Chloride of Aluminum, $AlCl_3$.—This compound is obtained by passing a stream of chlorine over a mixture of alumina and charcoal heated to redness in a porcelain tube. It is of a citron yellow color, translucent, crystalline, and stratified like talc. It is fusible, volatile, and very soluble in alcohol. It forms double salts with the alkaline, and even with sulphuretted and phosphuretted hydrogen.

Bromine and fluorine combine with aluminum.

The oxysalts of alumina are numerous and important from their various applications to the arts.

Sulphate of Alumina, $Al_2O_3 3SO_3$.—This is the formula of the neutral sulphate, which crystallizes in thin, flexible, pearly leaves, needles, and tables. There are several basic sulphates. The double sulphates with the alkalies are also numerous. The most important of these is the double sulphate of alumina and potassa, commonly called alum. This salt is transparent, color-

less, crystallizing in octahedra, combined with cubes and dodecahedra, the edges and pyramids being replaced by planes.

Silicates of Alumina.—There are numerous native and artificial combinations of this kind, both simple and double. Kaolin, for example, is $2(Al_2O_3,SiO_3)+3Ag$. Kyanite is $2Al_2O_3,SiO_3$, or $3Al_2O_3,2SiO_3$. Potash feldspar is $KO,SiO_3+Al_2O_3,SiO_3$. The formula for soda feldspar is the same, substituting Na for K. The micas are complex double silicates. We shall return to this subject again in a future chapter.

CHAPTER III.

POTASSIUM.

Potash being an important ingredient in the spar which is used in the manufacture of porcelain, a brief account of its chemical history is inserted here.

Its name is derived from the manner in which it was first obtained, by boiling down the leachings of wood-ashes in iron pots. The Germans call it kalium, a name which they get from the Arabic words *al kali*, or the kali, which term was originally applied to the ashes of sea-weeds. At first no distinction was made between it and soda, but about the middle of the last century, it was shown to be a different substance from the latter, and the names, vegetable and mineral alkali, were applied to the two oxides.

Potassium.—In 1807, Davy showed that potash was an oxide of the metal potassium, by decomposing the alkali through the agency of a powerful galvanic battery. Gay-Lussac and Thenard afterwards obtained it by igniting potash and iron turnings in an iron tube. Wöhler's modification of Brunner's plan, is to ignite a mixture of charred cream of tartar and charcoal in a wrought-iron flask, which is laid horizontally in the fire, an iron tube being screwed in the opening. The receiver consists of two copper vessels, the lower one open above and the upper one below,

and so arranged that the naphtha with which the bottom one is one-third filled, shuts out the air from the upper vessel. This has three openings towards its upper part, into one of which the tube is passed. Opposite it, is another, closed by a cork, which is from time to time removed, so as to thrust in an iron wire or auger, to clean out the tube when it happens to be stopped up. The third opening is designed for the escape of gases, and may be furnished with a tube, passing into a condenser, so as to collect the arsenic acid. The flask, being charged with the mixture already described, is now heated, and when green vapors begin to show themselves, the tube is connected with the receiver, and a strong heat applied. The tube must be bored, whenever it becomes clogged, and should this be impossible, the heat should be abated, for if an attempt should be made to open it, the ignited potassium would be driven out with an explosion. The operator must, therefore, stand on one side, and have his hands covered. When the operation is completed, the receiver is detached, all the openings being immediately stopped with corks. As soon as it has cooled sufficiently, the inner vessel is removed, its contents moistened with naphtha, and the potassium raked down into the naphtha. The black mass is either dissolved to obtain rhodizonate and croconate of potassa, or redistilled in a fresh operation. The metal is purified by redistillation. It is always kept in naphtha.

Potassium is a brilliant white metal, having a crystalline texture. Pleische obtained it in cubic crystals. It is a soft solid, beginning to melt at 70°, and becoming completely fluid at 136°. At 50° it is like wax in consistence, and at 32° it becomes brittle. In close vessels it sublimes in crystals. In the air it rapidly oxidates, becoming white and moist. Thrown on water it takes fire from the violence of the action, and burns with a violet light. Its affinity for oxygen is so powerful that it abstracts this metalloid from nearly all its compounds.

The specific gravity of potassium is 0.865. Its symbol is K. Its combining number is 39.11 on the hydrogen, 488.856 on the oxygen scale.

Potassa, KO. 47.11.—When potassium is heated in the air, dry potash is obtained. The *hydrates* are numerous. The most

important is the protohydrate, which is commonly obtained by treating pearlash with lime. To procure a pure hydrate of potash, it is necessary to make a solution of 3 parts of pure carbonate of potash in 12 parts of distilled water, and to add to it, while boiling, in small quantities at a time, milk of lime, made by slaking 2 parts of caustic lime with 6 of water. It is boiled after each addition of lime, and finally, when all is added, boiled for fifteen minutes. A little is then filtered off. Should it give no precipitate with lime-water, it may be regarded as pure.

Should a cloudiness be produced by this reagent, we are apprised that some carbonate of potash has been left undecomposed, and the whole is to be again boiled with milk of lime. When all the carbonate has been decomposed, the liquid is rapidly filtered, so as to expose it as little as possible to the air. Donovan's apparatus supplies a simple and very efficient means of accomplishing the desired result of excluding air as much as possible. When operating on large quantities, the clear solution is siphoned off from the sediment, and boiled in a clean iron kettle to the consistence of an oil. Should it become cloudy, it is again drawn off and allowed to settle in closely corked bottles; and, the clear solution being returned to the pots, the concentration goes on. The oily liquid is then evaporated in a silver dish till white vapors begin to rise from it. It is then poured into moulds, or on slabs, when it is solidified. During the evaporation, carbonate is formed, which floats on the oily liquid, and may be skimmed off. It may also be obtained by treating sulphate of potassa with pure baryta water, and evaporating as just described.

The ordinary potash of the shops, however beautiful and white it may look, always contains some chloride, and occasionally a little carbonate. It is made of pearlash, which is never an absolutely pure carbonate.

Fused potassa (*potassa fusa*, *lapis causticus*, or caustic potash of the shops) is the protohydrate of potash, containing 84 per cent. of dry potassa. It is the form in which this alkali is usually seen, and was formerly supposed to be pure and anhydrous. It is perfectly undecomposable in all known heats. It fuses below redness, and volatilizes at higher heats. It has a

powerful affinity for water, deliquescing rapidly in the air, and dissolving in one-half its weight of water with the evolution of heat. Even when quite dilute, it has a peculiar smooth, soapy feel, when rubbed between the fingers. This is due to its action on the epidermis, the scales of which it dissolves.

In the solid form, potassa is a powerful escharotic, and is largely used by the surgeon. The dentist occasionally employs it for the destruction of the exposed nerves of the teeth. Its action is violent, and accompanied with much pain. This may be, to some extent, moderated, by making it into a paste with alcohol and morphia.

Our space does not permit us to dwell upon the other non-saline compounds of potassium. Of the salts, there are few of special interest to us. We shall describe only the

Nitrate of Potassa, KO,NO_5.—This salt is generated spontaneously in some soils, and crystallizes upon their surface. It is easily obtained from them by lixiviating them and crystallizing the clear solution. The East Indies yield the greatest portion of this substance, though it occurs elsewhere in soils. It is more commonly found native as an efflorescence on certain rocks, and as a saline crust in caverns. In Tennessee and Kentucky, especially in the latter State, native nitre is so abundant in caverns as already to have become a considerable article of traffic.

Some plants have the property of generating nitre from the constituents of ordinary soils. Among these is tobacco; and few persons have resided any length of time in a tobacco-growing country who have not observed crystals of this salt occasionally formed in the axils of the leaves. Maize is also said to form it.

The formation of nitre in soils, and on the surface of rocks, has been variously explained. It has been supposed that the animal matter present in soil and calcareous rock becomes oxidated at the expense of the atmosphere, so that its nitrogen is converted into nitric acid. Deliquescent nitrates of lime and magnesia result; and these, in their turn, are decomposed by the potash which is present in the soil. This generation of

nitre, both in soils and rocks, is limited to a very small distance from the surface of porous stones.

Dr. John Davy and M. Longchamp suppose that azotized matter is not absolutely necessary; but that the oxygen and nitrogen of the atmosphere, when condensed by capillary force, combine in the proportions necessary to produce nitric acid, which, when formed, attacks the magnesia and lime, and is afterwards abstracted from the salts of these bases by potash. They believe the action of the porous limestones and the water in them, in this case, to be analogous to that of spongy platinum in condensing oxygen and hydrogen into water; or of sesquioxide of iron and argillaceous substances in combining nitrogen and hydrogen to form ammonia. Plausibility is given to this opinion by the fact that, in India, Spain, and other nitre-producing countries, this salt is generated in places remote from all human habitations, and, to all appearance, secluded as completely as possible from all organic influences.

During the wars of the French Revolution, England, having possession of the sea, shut out from the ports of France all the Indian and other foreign nitre. This struck at the nation's vital part, by cutting off the supply of the most important munition of war. The genius of the French chemists, however, overcame the difficulty by establishing artificial nitre-beds, from which the manufactories of gunpowder were liberally supplied.

These *nitrières artificielles* are made by using as the basis a light, porous earth, freely permeable by atmospheric air, and containing a large proportion of carbonate of lime or old mortar rubbish. This is interstratified with beds of dung, five or six inches thick, and the whole mass raised into a truncated pyramid, which is kept moist by constant watering. When the whole has been decomposed into a sort of mould, it is placed in layers under a shed, watered with urine and the drainings of the stable-yard, taking care not to soak them so much as to obstruct the free entrance of atmospheric air, and at the same time to keep them moist enough to furnish ample means for the absorption and combination of the atmospheric gases. The beds are freely turned over thoroughly to mix their contents and to favor the combination of the nascent acid with the bases. Two years are

necessary to complete the process, during the latter six months of which period the organic liquids are disused and pure water substituted in the watering process. Longchamp suggests that this manufacture be carried on in forests, where fuel and labor are cheap, that organic matters be disused, and that *tuf* be employed to condense the gases.

Most of the indigenous nitre of France is obtained from old mortar and plaster, especially that of the ground-floor and cellars. This is lixiviated in large casks, and the solution obtained from their lixiviation is evaporated and mixed with sufficient wood-ashes to substitute potash for lime as a basis of the nitrates. The chloride of sodium collects on the surface during the concentration of the nitre, and is skimmed off in ladles. The concentrated solution is siphoned off, crystallized, and purified sufficiently for commercial purposes by one or two recrystallizations.

Nitrate of potash is a colorless salt, crystallizing in six-sided prisms with dihedral summits. They are grooved, and in the cavities are liable to contain mother water. The specific gravity varies from 1.93 to 2. Its taste is cool and saline. It is inodorous, permanent in the air when pure, fusible at 662°, concreting from the fluid into a solid mass, with a coarsely radiating fracture, which has received the names of *sal prunelle* and *mineral crystal.* If the heat be raised to ignition, a portion of the salt is decomposed, oxygen being given off, and nitrite of potassa remaining. Owing to this property, it is a powerful oxidating agent in metallurgy. For the same reason, it deflagrates violently on ignited coals, when heated to redness with sulphur. It is soluble in 7 parts of water at 32°; in about $3\frac{1}{2}$ at 60°; in less than half a part at 194°; and in four-tenths at 212°.

It is a substance of almost universal application in the arts. It is essential to the manufacture of gunpowder, of sulphuric and nitric acids, and of flint-glass. It is used also in medicines, and in many chemical and pharmaceutical operations.

CHAPTER IV.

SODIUM.

THERE are soda as well as potassa feldspars, so that a brief account of the behavior of soda is here inserted.

Sodium, as well as potassium, was discovered by Sir Humphry Davy, in 1807. It is obtained in the same manner as potassium, which it resembles in color, lustre, and mode of crystallization. At common temperatures, it is so soft that it may be formed into leaves by the pressure of the fingers. At 4° F., it is hard; at 32°, malleable; at 122°, very soft; at 194°, fluid, and at a red heat, vaporizable. It oxidates readily in the air, though not so rapidly as potassium. It is rapidly oxidated by water, throwing off hydrogen and steam. In hot water, it scintillates, but does not burn like potassium. Ducatel says that the heat rises high enough to inflame the sodium, even in cold water, provided the metal be confined to one place, and the water rest on a non-conducting base, like charcoal.

The specific gravity of sodium is 0.972. Its symbol is Na; its combining number, 23.3 on the hydrogen, and 289.729 on the oxygen scale.

Soda, NaO. 31.3.—Dry soda, absolutely anhydrous, is made by burning the metal. It is a gray mass, which fuses at a strong red heat, and absorbs water greedily with evolution of heat.

Hydrate of Soda, NaO,HO.—Water added to dry soda is rapidly absorbed, and hydrate is formed. It is usually obtained by the action of caustic lime upon the best soda-ash. The two substances are mixed in the proportion of 48 parts of quicklime to every 100 of alkali present in the ash. It is a white, brittle, fibrous substance, fusible and slightly volatile at a full red heat. It may be obtained in crystals by evaporating a concentrated solution at a very low temperature.

The salts of soda are numerous and interesting, but our limits

will suffice only for the description of the two which are chiefly used as fluxes, the *carbonate* and the *borate*.

Carbonate of Soda, NaO,CO_2.—The impure carbonate of soda of commerce, called soda-ash, is obtained from common salt by a somewhat complicated process. The salt is first decomposed by the action of sulphuric acid at a high temperature. Hydrochloric acid is given off, and sulphate of soda remains. The sulphate is powdered and mixed thoroughly with excess of chalk, or carbonate of lime, and some charcoal, also in fine powder. The mixture is then fused, and ball-soda, or crude soda, is obtained, which is a mixture of carbonate of soda, and caustic soda with sulphuret of calcium, carbonate of lime, charcoal, undecomposed sulphate, &c. This crude soda is lixiviated in a series of cisterns, so arranged that the lowermost shall contain a concentrated solution of the alkaline carbonate, while the higher shall have in it nearly pure water, to exhaust the last remains of alkali from the crude mass. The lye of the lowest cistern is concentrated, during which process it lets fall crystals of carbonate of soda. These are lifted out and drained, while the remaining liquid, which contains caustic soda and sulphuret of sodium, is evaporated to dryness, mixed with charcoal or sawdust, and heated in a reverberatory furnace till all the sulphuret is decomposed. Sometimes the crystals are not separated, but the whole solution is evaporated to dryness, and treated as just described. The resulting compound is the *soda-ash* of commerce.

From this the pure carbonate is obtained by repeated crystallizations. Its crystals always contain water, the amount of which varies with the temperature at which the crystallization has been effected. For the purposes of fluxing, this water should be expelled by heating the crystals to a low redness in a perfectly clean wrought-iron crucible. A snowy-white agglutinated mass is obtained, which is easily reduced to an impalpable powder. In this form, it is one of the most valuable reagents, in the dry way, possessed by the chemist, and one of the most important of all the metallurgist's fluxes. It possesses the power of decomposing the silicates, the silicic acid of which, at a high heat, unites with the alkali, expelling the carbonic acid. During the fusion, the escape of the last-named acid, in a gaseous

form, causes a violent ebullition, which will throw out all the contents of the crucible, if the latter is not sufficiently capacious. When this ebullition has ceased, and the surface of the melted mass has become bright and smooth, the fusion is complete. Besides this, carbonate of soda forms fusible compounds with most of the metallic oxides, and retains in suspension, without losing its fluidity, a great number of infusible substances, such sa charcoal and the earths. This substance also, at a high temperature, oxidates some metals. The carbonic acid which it contains is partially decomposed into carbonic acid, which escapes, and oxygen, which combines with the metal.

Borates of Soda.—There are two borates of soda, the neutral borate (NaO,BO_3) and the biborate ($NaO,2BO_3$). The latter is the salt used as a flux.

The biborate of soda is manufactured from the native boracic acid formed in such abundance in the lagoons of Tuscany, or is imported as a crude impure article, under the name of *tincal*, from Asia and South America. The crude boracic acid from the lagoons, is saturated with carbonate of soda, and crystallized at 92°. Repeated crystallizations purify the salt. If these are made at a temperature lower than 130°, the crystals assume the form of oblique rectangular prisms. If crystallized at 130°, octahedral borax is obtained, mixed with the common crystals.

Borax has an alkaline reaction, and a cool, faintly saline taste. When exposed to the air, the superficial layer of its crystals loses water and effloresces. Heated moderately, it loses water, and is greatly increased in bulk, being converted into a loose, light, white mass. If the heat be now increased, it fuses gradually to a transparent colorless glass. To one or the other of these forms it should be reduced, before it is used as a flux; otherwise its property of swelling, as it loses its water, would be productive of great inconvenience, and might even completely defeat the object of the manipulator. The glass is the best form of flux, and it has the advantage also of keeping better, as it does not absorb water from the air so readily as the loose, spongy variety.

Borax has been called a universal flux, and it fully deserves the appellation. It forms fusible compounds with silica and

nearly all the bases. Its solvent power and that of its acid have recently been made use of to obtain artificial silicious, and other earthy crystals.

CHAPTER V.

THE MATERIALS USED FOR PORCELAIN TEETH.

CLAYS.

The clays constitute a very extensive geological formation. Clay, or aluminous minerals bearing that name, enter into the composition of many of the older rocks, but those used in the arts are of modern formation. These strata are characterized by a very minute division of their particles, and a want of solidity. They are easily suspended in water, with which they form a dough, and it is to this property we owe their very general distribution. They have, in all cases, been deposited from still or running water. Their origin has undoubtedly been from disintegrated rocks. In many places, the process of the formation and deposit of clays may be seen even now going on. Porcelain clay, or kaolin, being found surrounded by the rocks, from which it was formed, offers the most favorable opportunity for the solution of the problem of the formation of these deposits.

It was first ascertained that all species of kaolin were formed by the decomposition of feldspathic minerals by the atmosphere. On examining the kaolin, however, a manifest diversity in the physical character of its component parts was discovered. A portion of it only was the real *plastic clay*, as it is termed. The rest was found to consist of fragments of undecomposed rock, of free silicic acid, and silicates of the alkaline earths. The rocky debris may consist of substances capable of generating clay, but which have not been sufficiently disintegrated, or of earths which cannot undergo that transformation. There is also

a soluble silica present, which has combined with bases during the process of decomposition.

To examine porcelain earth, therefore, the soluble silica must first be removed, by boiling it for a minute or two with a solution of potash containing about 20 per cent. of the alkali. The clay can then be separated, by boiling it first with sulphuric acid and afterwards with potash. The alumina, together with the alkalies and earths, when they are present, is held in solution by the sulphuric acid, and the silica by the potash, the undecomposed rocks remaining as residue. The clay, rejecting the earths, is found to be composed according to the formula M_2O_3,SiO_3+2Aq, in which M represents the metallic base, usually aluminum. Feldspar has the formula $M_2O_3,3SiO_3+MO,SiO_3$, the letter M representing usually potash, soda, or an alkaline earth. A comparison of the formulæ, will throw light on the processes concerned in the formation of porcelain earth:—

Feldspar $= M_2O_3+4SiO_3+KO$ is decomposed into porcelain-clay $= M_2O_3+SiO_3$, into an insoluble silicate of potash $= 3SiO_3+KO$, when the feldspar contained potash, or silicate of soda $= 3SiO_3+NaO$, when soda was the base of the mineral.

These silicates are still farther decomposed; the latter parts with SiO_3, and becomes the soluble bisilicate of soda, $NaO,2SiO_3$, while from three equivalents of the former, $3KO,9SiO_3$, the same amount of silica is separated, leaving the soluble compound, $3KO,8SiO_3$. In time, these soluble salts are removed by the action of water. The rapidity with which this will be effected, will depend, of course, upon the length of time the clay has been subjected to these decomposing agencies, and the freedom with which the water has had access to it. The alkaline earths, if present in the rocks, are usually found mixed up with the clays.

An examination of a very large number of specimens of kaolin, leads to the adoption of the formula Al_2O_3,SiO_3+2Aq for the great majority of these clays.*

Clay is, as we have already said, pulverulent when dry, and

* Knapp's Chemical Technology.

emits a peculiar odor, termed *argillaceous*, when breathed on. When moistened, it forms a mass, communicating usually an unctuous sensation to the touch, and capable of being moulded into almost any desired form. When dried, it shrinks very much, and usually cracks, as may be seen in any sun-baked clayey soil. When dried at ordinary temperatures, water can again convert it into the same soft yielding mass. When exposed to a very intense white heat, it does not fuse, but all its characters are changed. It is, indeed, still porous, and continues to absorb water, but this liquid has no longer any action upon it. Its particles now adhere strongly to one another, and it becomes hard and sonorous. Laurent has shown that clay goes on increasing in density till it arrives at a cherry red heat, and that after that its specific gravity diminishes, till at an intense white heat it is no higher than it was at 212° F.

These properties of the clay will, of course, be modified, and often seriously impaired by the foreign matters which are usually found in them. The variety of these foreign substances has already been mentioned. In a yellow clay of Denmark, of granitic origin, Foschhammer found, in the *granite*, feldspar, quartz, mica, magnetic iron, oxide of titanium, and compounds of cerium; in the clay, kaolin, sand, mica, oxides of iron and titanium, and compounds of cerium.

Here the clay came from the feldspar, but was mingled with the quartz or sand and with the mica, while the magnetic iron was farther oxidated, and mixed with the titanium and cerium present in the granite.

Among these foreign substances, those which exert the most unfavorable influence over the clay are *sand* (composed of quartz and decomposed minerals), *iron*, *lime*, and *magnesia*. They all diminish its plasticity, sand interfering with it the most, and iron the least. Lime or iron mixed with clay, entirely changes its relations to heat. It becomes fusible, and melts with greater or less readiness, as it contains more or less of these ingredients. Magnesia has little effect upon clay, and sand diminishes its fusibility, as well as the extent of its contraction.

Brogniart has divided the clays into four varieties: the *fireproof*, the *fusible*, the *effervescing* or *calcareous*, and the *ferru-*

ginous or *ochrey*. Of these, there is but one variety to which we need direct our attention at present, the *fire-proof*.

Kaolin, or *Porcelain Earth*.—The name *kaolin* is the Chinese *kao lin* or *kauling*,* and has been adopted in all European languages. It is an earthy, white or grayish mineral, easily pulverized, and containing usually foreign substances mixed with it. It is friable in the hand, and is with some difficulty formed into a paste with water. It is usually found in primitive mountain districts, among blocks of granite rich in feldspar, but poor in mica, upon porphyry and the more recent feldspathic rocks. In consequence of this origin, most of the kaolins contain a few spangles of mica diffused through them, not to be separated by washing.

The principal localities of kaolin, on the eastern continent, are, in Asia—China and Japan; in Europe—St. Yrieux-la-perche, near Limoges and Bayonne, in France; Miessen, Halle, and Passau, in Germany; and St. Anstle, Cornwall, in England. In the United States, kaolin has been found near Wilmington and Newcastle, in Delaware, and in Chester County, Pennsylvania. It also occurs at Andover, Massachusetts; and abundantly in New Milford, Kent, and Cornwall, Connecticut; and in Essex and Warren counties, New York. Good kaolin is also found in the vicinity of Baltimore.

The kaolin of St. Yrieux, used in the famous manufactory of Sèvres, has been found by Berthier to contain in the 100 parts:—

Silica	47.09
Alumina	36.41
Potash	1.56
Magnesia	2.94
Water	12.00

The Cornish *China clay* is artificially prepared by passing a stream of water over decomposed granite. This carries off the finer particles of feldspar, which are received, together with the

* Meaning *high ridge*, the name of a hill near Jauchan Fu, where this mineral is obtained. *Pe-tun-tze*, with which the Chinese mix their kaolin for their porcelain manufactures, is a quartzose feldspathic rock, consisting mainly of quartz.

water, in cisterns or ponds, where the mineral is allowed to subside. The water is then drawn off, and the fine sediment is removed, and exposed to the atmosphere for four or five months, when it is ready for use. Richardson's analysis of a specimen of this clay gave—

Silica	46.32
Alumina	39.74
Protoxide of iron	.27
Lime	.36
Magnesia	.44
Water and some alkali	12.67
Loss	.20
	100.00

From a table of analysis by Brogniart and Malaguti, published in Knapp's *Chemical Technology*, we extract the following estimate of the clays of Newcastle and Wilmington:—

	Wilmington.	Newcastle.
Rocky portion insoluble in potash and acid	22.81	34.99
Lime, magnesia, and potash	1.14	
Soda	.72	
Iron and manganese	trace	trace
Silica separated by potash	12.23	9.39
Silica in combination with alumina	20.46	20.34
Alumina	35.01	25.59
Water	12.12	8.94

FELDSPAR.

Under the general name *feldspar*, have been confounded a great variety of minerals, which, while differing in details, agree in general conformation, geological situation, and to a certain extent in external appearance. They are found universally in granite, trachyte, porphyry, and other plutonic rocks, as a necessary and natural ingredient. They are also found in veins or masses penetrating or imbedded in these rocks.

They all crystallize in the oblique rhombic and doubly oblique

rhombic (monoclinate and triclinate) systems. It is remarkable that the triclinate feldspars abound in soda and lime, while those of the monoclinate system contain a larger quantity of potassa. The feldspathic minerals are also analogous in their chemical constitution, all of them being double silicates of alumina, and some alkali or alkaline earth. Their lustre is either pearly or vitreous. Their color varies, being red, gray, greenish, flesh-colored, roseate, pure white, milky, transparent, or translucent. They lose no water when ignited; and, at a high heat, are glazed on the surface, or fused to a transparent glass full of bubbles. Acids do not attack them; caustic alkalies affect them but slightly, and then mainly upon the surface, when the action of air and moisture has produced incipient decomposition.

Analysis has shown the composition of the great majority of feldspars to be $Al_2O_3,3SiO_3+Ko,SiO_3$. The potash is often replaced, in whole or in part, by soda, lime, lithia, or magnesia, and a portion of the alumina by sesquioxide of iron.

Adularia is a beautiful transparent variety of feldspar, usually found in granite. It occurs at Haddam and Norwich, Conn.; Brimfield, Mass.; and Parsonsfield, Me. Its composition, according to Berthier's analysis, is:—

Silica	64.20
Alumina	18.40
Potassa	16.95
Loss	.45
	100.00

Glassy feldspar is usually found in trachytic rocks, and contains a notable proportion of soda, as may be seen by the following analysis by Berthier, of a specimen from Mont d'Or:—

Silica	66.1
Alumina	19.8
Potassa	6.9
Soda	3.7
Magnesia	2.0
Loss	1.5
	100.0

Common feldspar includes a number of subtranslucent varieties. We subjoin two analyses, by Booth and Boyé; the first, of a massive, highly translucent variety, found about six miles north-west of Wilmington, in Delaware; the second, of a bluish and smoky feldspar, from the Brandywine quarries of blue rock, a few miles north-east of Wilmington, Delaware. The specific gravity of the first was 2.562; of the second, 2.603:—

Silica	65.24	66.51
Alumina	19.02	17.67
Potassa	11.94	9.81
Soda	3.06	3.03
Lime	.33	1.24
Magnesia	.13	.30
Oxide of iron, &c. . . .	trace	1.33
Loss	.28	.11
	100.00	100.00

Albite is one of the soda-feldspars. It is whiter and more pearly in its lustre than common feldspars, and belongs to the triclinate system of crystallization. Sometimes, but rarely, it is pale bluish, greenish, grayish, or reddish, and may be either transparent or opaque.

It often replaces feldspar in granite, sienite, &c., and is found in Delaware, associated with common feldspar, from which it is distinguished by its more pearly lustre. It resembles feldspar in its chemical reactions. Its specific gravity varies from 2.6 to 2.68. We subjoin two analyses of American albite by Booth and Boyé; the first, of a crystalline and granular specimen, from Chester County, Pennsylvania; the second, of a highly crystalline piece, from the vicinity of Wilmington, Delaware:—

Silica	67.72	65.46
Alumina	20.54	20.74
Peroxide of iron . . .	trace	0.54
Magnesia	0.34	0.74
Lime	0.78	0.71
Soda	10.65	9.98
Potassa	0.16	1.80
	100.19	99.97

It is hardly necessary to say that only the whitest varieties of this mineral can be used in the manufacture of porcelain. It is employed both for body and glaze.

QUARTZ SAND.

Quartz is another of the granitic minerals, and has of course a very extensive distribution over the surface of the earth.

It crystallizes in the hexagonal system, usually in prisms, terminated by six-sided pyramids. It is also found granular and compact, rarely fibrous. When perfectly pure, it is colorless or white, depending upon the arrangement of its particles. Its lustre is vitreous, rarely resinous; and its fracture usually conchoidal. It is generally contaminated with foreign substances; of which alumina, the alkaline earths, and the metallic oxides are the most common. The latter communicate to it the different colors characteristic of its varieties.

Rock crystal is the purest variety. It is perfectly colorless and transparent, hard, and infusible. It is insoluble in every acid but the hydrofluoric. The crystallized variety is with difficulty attacked by caustic potassa; the amorphous much more easily. When used in the manufacture of porcelain, it is first heated to redness, then quenched suddenly in water, and reduced to a fine powder by levigation with water.

These are the materials used in the manufacture of the body and glaze of porcelain. The colors are given to it by the metallic oxides, which will be described after we shall have examined the structure of porcelain.

CHAPTER VI.

PORCELAIN.

The beautiful white ware to which the name of porcelain has been given, was unknown to those nations we commonly call the ancients. To the stationary people of China, however, it is an

old article of manufacture, having been made in that remote empire many centuries before the advent of Christ. It was first introduced into Europe by the Portuguese, from whose language the term *porcelain* is derived. This term *porcellana* is supposed to have been originally applied to the porcelain-shell, and transferred to the ware on account of its resemblance to that beautiful production of nature. The name *China*, by which this fine pottery is still known, points out the country in which it originated, and from which it was first imported by the occidental nations. It was very imperfectly imitated in France in the seventeenth century.

The first European manufacturer of porcelain was Bötticher, a German, the founder of the famous manufactory of Meissen. Addicted to alchemical pursuits, he got himself into trouble with the kings of Prussia and of Poland, who attempted to force out of him the secret of gold-making, which he professed to possess. At last, such rigorous measures were adopted that he was compelled to confess his ignorance of the philosopher's stone, but endeavored to appease Augustus II., of Poland, who had him in prison, by assuring that monarch that he was acquainted with the art of porcelain manufacture. He had, indeed, made a red stoneware very nearly allied to porcelain, and, after many experiments, carried on in his prison, he succeeded, in 1709, in producing the true white porcelain. He died in 1719.

The art spread slowly from Saxony. In 1720, it was introduced at Vienna; in 1751, at Berlin; in 1755, at Nymphenburg, near Munich; in 1758, at St. Petersburg; and in 1765, after the kaolin of St. Yrieux had been discovered, it superseded the tender porcelain at Sèvres, near Paris.

There are two substances which have received the name of porcelain; the *tender porcelain*, or *iron-stone China*, of the French and English—which is only a vitreous frit containing substances of difficult fusibility—and the *hard* or *true porcelain*, consisting of burnt clay and a flux of quartzose feldspar.

English tender porcelain approximates much more nearly to true porcelain than the French ware. It is made of plastic clay; kaolin from Cornwall; Cornish stone, a mixture of quartz, kaolin, and undecomposed feldspar; burnt bones; chalk flints, and steatite.

The latter substance is said to diminish the contraction of the wares during the baking. These materials are ground finely, elutriated, and mixed with a frit composed of Cornish stone, flint, soda, borax, and oxide of tin. The ware is twice fired, and the temperature of the oven is regulated by small trial pieces, which are withdrawn from time to time. The glaze resembles the frit in its composition, with the addition of carbonate of lime and some lead.

Recent analyses of English china make its composition: silica, 40.60; alumina, 24.15; lime, 14.22; protoxide of iron and phosphate of lime, 15.82; magnesia, .43; alkali and loss, 4.78.

The *true porcelain* has the kaolin for its basis, which, being a plastic clay, is easily moulded into any desired form. Kaolin alone, however, would turn to a porous, opaque body; a flux is therefore introduced, which consists of feldspar, chalk, gypsum, broken porcelain, or some such material. This, while it prevents the kaolin from shrinking out of shape, assists in vitrifying the mass.

It is essential to the beauty, and, indeed, to the very existence of good porcelain, that these different ingredients should be reduced to the finest possible state of division, and mixed in the most intimate manner. For this purpose, mills are used, and the ingredients elutriated separately, and mixed while they are still in the condition of a soft, thin mud. The proportion found at Sèvres to yield the best results is: silica, 58; alumina, 34.5; lime, 4.5; potash, 3. The wet pastes are mixed in this proportion by measurement, the weight of dry matter in a given bulk of mud having been previously ascertained. It must be remarked, however, that it is by no means certain that such a mixture as that of Sèvres will always yield porcelain of the same quality, since very much depends on the manner in which the proximate elements of the paste are combined.

The paste thus obtained must be dried to a mass that can be easily kneaded. Numerous difficulties are here to be overcome. It must not be dried too fast, or it will lose plasticity, nor can it be allowed to drain, as the heavier particles will sink to the bottom, and the uniformity of the mass be destroyed. The old

method of overcoming this was to draw off the mixture into boxes with bottoms of plaster of Paris, which absorbed the moisture. Another method, which has superseded the last, is to subject the mud to strong pressure; while another very elegant plan has been suggested, making use of atmospheric pressure. The paste is thrown on thick layers of felt, resting on metallic sieves, which are adapted to iron funnels. These terminate in an iron tube communicating with a close chamber, from which the air can be easily exhausted. The weight of the atmosphere then forces the fluid through the pores of the felt, and a rapid filtration is accomplished.

The pliancy of the mass is greatly increased by the process of *mouldering*. This consists in beating up the paste in small balls, and laying them aside in a damp place, where the organic matter they contain ferments. A fetid smell is emitted, the centre of the lumps become black, but lose that color as the air penetrates them. It is difficult to account for the increased pliability of the mass in consequence of this process, but it is so well understood by practical men, that they are in the habit of mixing honey, syrup, and other organic matters with their clay, in order to facilitate the change.

The paste thus prepared is moulded, cast or carved into the desired form, and the different articles made from it are dried in the shade till they cease to lose weight. They are then burned slightly, preparatory to putting on the glaze. The ware after this first firing is called *biscuit*.

The glaze of porcelain is a glass entirely free from lead. In some places, it is composed of kaolin, gypsum, and broken porcelain, so that it is a glass containing alumina and lime, with the small quantity of potash contained in the old porcelain. At Sèvres, the glaze is composed of the pegmatite* from St. Yrieux, and consists, therefore, of quartz and feldspar. The average proportions of Sèvres glaze are silica, 74; alumina, 17, and potash, 9, with a little lime and magnesia. The proper fusibility of the glaze is an exceedingly important point to arrive at. Should it be not sufficiently fusible, it will not form an even surface, but will appear wavy. Should it be too fusible, it will melt before

* Graphic granite.

the body is sufficiently baked, sink into the porcelain, and leave the surface rough and dry. To insure the uniform distribution of the glaze over the surface of the ware, the article to be glazed is dipped into a tub containing the materials suspended in water.

Porcelain is milk-white, without any tinge of blue. Its value depends upon the closeness of its texture and the intimacy with which its hard glaze is connected with the body. The manner in which its two component parts, the kaolin and the flux, are connected with one another has been variously explained. It was formerly supposed that the kaolin remained a sort of infusible skeleton, through which molten feldspar or other flux was poured, giving translucency to the mass, as opaque paper is rendered transparent by being saturated with varnish. According to the recent microscopic observations of Oschatz and Wächter, however, the porcelain mass consists of a vitreous matrix, intersected in all directions by minute needle-shaped crystals ; the want of transparency being due to the reflection and refraction of light among these minute crystalline particles.

Porcelain undergoes a notable diminution of volume during the process of baking. The slightest variation in the component parts of a paste will alter this *shrinking*, but in the same paste the contraction is constant, so that it can be estimated with great accuracy. The average *linear* contraction is 13 per cent.; this may, however, fall to 7 or rise to 17 per cent. The average contraction in *volume* is stated at 39 per cent.

The *density* is increased with the contraction. The specific gravity of the dry mass, once heated, is 2.305 ; after thorough baking, it is 2.478. This is taken from the mass, and therefore includes the pores. It is remarkable, however, that, when reduced to powder, its specific gravity diminishes with the increase of temperature to which it has been subjected. Thus, according to Malaguti, the powder of once heated porcelain had a specific gravity of 2.619 ; of half-baked, 2.44 ; thoroughly baked, 2.242. It has been supposed, in order to account for this phenomenon, that while the particles themselves are expanded, they are brought in closer proximity to each other, and thus, while the specific gravity of individual particles is diminished, that of the mass is increased.

A number of analyses of porcelain have been published. We select three; the first, of Sèvres porcelain, by Laurent and Malaguti; the second, of Berlin ware, by Cowper; and the third, of Chinese, by the same chemist.

	1.	2.	3.
Silica	58.0	72.96	71.04
Alumina, with a little protoxide of iron . . .	34.5	24.78	22.46
Lime	4.5	1.04	3.82
Alkali	3.0	1.22	2.68
	100.0	100.00	100.00

CHAPTER VII.

COLORING MATERIALS.

The art of tinting porcelain depends upon a knowledge of the management of the vitrifiable pigments. Like all other pigments, they may be mixed so as to produce a very great variety of tone and tint, but, unlike common coloring matters, chemical changes and reactions take place among them at the high heat to which they are necessarily exposed, so that the artist must take into account not only the effects of the blending of colors, but also the chemical modifications of the components of his palette.

The number of colors used by the manufacturer of porcelain teeth is not large. He has not those varied and brilliant tints to apply which the artist at Sèvres or Meissen requires for the production of his beautiful pictures. His tints are few and undecided; but the very vagueness, delicacy, and indistinctness of them, demand close attention, and no little knowledge of the subject. These colors are various shades of gray, yellow, and rose, obtained sometimes directly, sometimes by the blending of more positive tints.

The principal oxides and metals used and the colors they produce are given on the next page.

Metals and Oxides.	Colors produced.
Platina sponge or black, . .	Grayish-blue.
Platino-chloride of ammonium,	Blue.
Gold, in a state of minute division,	Rose red.
Peroxide of gold, . . .	Bright rose red.
Purple of Cassius, . . .	Purplish rose color.
Oxide of titanium, . . .	Bright yellow.
Oxide of uranium, . . .	Greenish or orange yellow.
Oxide of zinc, . . .	Lemon yellow.
Oxide of silver, . . .	" "
Oxide of cobalt, . . .	Brilliant blue.
Oxide of manganese, . .	Purple.

In the above table, the metals and oxides are regarded as perfectly pure. Any deviation from absolute purity will of course modify the tint. Thus the oxide of titanium commonly used is not pure, but contains iron. The consequence is that the bright yellow tint of the pure oxide is not obtained, but a dingy tint far better suited to the purpose of the manufacturer, who desires to imitate the dusky yellowish color of many teeth.

Desirabode's tints differed somewhat from these, and most of them are now generally abandoned. He obtained his blue from cobalt, his gray from platina and mercury, his violet and red from gold, his bluish-gray from bismuth, his pale yellow from silver, his brownish-yellow from iron, his purple gray from manganese, his straw yellow from uranium and titanium, and his pure yellow from antimony. Of course, he blended these positive colors so as to get a subdued tint.

In the preparation of the above colors, much care and no little chemical knowledge are required to get accurate results. Many of them demand a very complete acquaintance with the reactions of the metals and the chemical modes of separating them. To get many of them in a state of purity, a careful analysis of the ores of the metal sought for is required, and then great skill and delicacy are necessary in the manipulations. Unless, therefore, a manufacturer possesses the necessary knowledge, it is much better that he should purchase his oxides from a competent chemist than trust to the chances of his own

success. The following directions, however, will assist those who desire to get a personal experience in these manipulations.

Platina sponge and *platino-chloride of ammonium* have already been described.

Gold, in a minute state of division, is obtained, as already directed, by precipitating the chloride with protosulphate of iron, and washing the blackish powder, first with hydrochloric acid and then with distilled water. It is also prepared by grinding filings or foil with a little spar on a mortar or a marble slab. Another process is to melt in a crucible with borax 12 parts of pure silver, 4 of gold, and 1 of tin. The alloy is either granulated or rolled out in foil, and then treated with nitric acid, till all the silver is taken up. The residual gold is then thoroughly washed.

This process does not give pure metallic gold. There will always be a little silver and a notable quantity of oxide of tin mixed up with it.

Another very convenient way of obtaining finely divided gold is to throw it down from the chloride with oxalic acid. The best process is that with protosulphate of iron, if due care is taken to free the solution of the chloride from nitric acid before precipitating, and if the iron be thoroughly washed out of the precipitated gold.

The *peroxide of gold* is best made as already described. The more common method is to precipitate the gold with ammonia. The yellow precipitate obtained in this way, however, is not an oxide but a mixture of the oxide with ammonia and chlorine.

The *purple of Cassius* has already been described.

TITANIC ACID, TiO_2.—OXIDE OF TITANIUM.

This is found native in various degrees of purity. Its principal ores are *sphene*, *rutile*, *titaniferous iron*, *anatase*, and *brookite*.

Sphene, called also titanite and menachan ore, is a silico-calcareous oxide of titanium, or a silicate and titanate of lime. Rose's formula for it is $3CaO,SiO_3+2TiO_2,SiO_3$; Berzelius's $2(CaO,SiO_3)+CaO,3TiO_2$. It crystallizes in oblique rhombic

system. Its colors are various shades of yellow, green, brown, gray, and black; its lustre is adamantine resinous. It is brittle, and either transparent or opaque. Its streak is white. Before the blowpipe, it fuses on the edges, with some puffing, to a dark glass, dissolves in borax with a yellow color, with difficulty in microcosmic salt. Tin reduces it, giving first a yellow and then a violet tint to the bead. It occurs in primary rocks in many places, but rarely in masses.

Rutile crystallizes in prisms terminated by octahedra, and often twinned by turning 180° on an octahedral plane. Its colors vary from brownish-red to dark brown; its lustre is metallic or adamantine; it is subtransparent or opaque; its fracture is subconchoidal and uneven, and its streak light brown.

By itself, it is infusible, but with borax it gives in the outer flame a greenish, in the inner a violet glass. In the inner flame, with microcosmic salt, it gives a red glass, and sometimes, with the addition of tin, a blue or violet one. It fuses with soda, with effervescence, to a bead which sometimes shows manganese. When treated with soda, it usually shows tin. It is titanic acid, combined with more or less oxide of iron.

It occurs in primary rocks and in older limestones. In Lancaster County, Pennsylvania, very large crystals are found.

Anatase, octahedrite, oisanite, or pyramidal titanium ore, occurs in small octahedral crystals belonging to the tetragonal system. Its color is blue, passing into brown, red, black, and greenish-yellow, by transmitted light; its lustre is splendent and submetallic; its streak, grayish-white. It is either translucent or opaque. Heat makes it phosphoresce, for a moment, with a reddish-yellow light. Its blowpipe reactions are those of pure titanic oxide.

Brookite crystallizes in right rhombic prisms. Its color is hair-brown, passing into orange; its lustre, brilliant metallic adamantine; its streak pale yellowish. It is brittle, and either translucent or opaque. It is found at Phœnixville, near Philadelphia.

Titaniferous or *titanic iron* (Iserine, Menakan, &c.) crystallizes in rhombs with large end planes belonging to the hexagonal system; but is usually found in plates or grains. It is more or

less magnetic, opaque, iron black, with a submetallic lustre and a conchoidal fracture. It is infusible by itself, and gives reactions of both iron and manganese with the fluxes. With microcosmic salt, in the inner flame, it gives a reddish glass, which tin either decolorizes or renders violet. Aqua regia takes up the iron and leaves titanic acid. It is usually supposed to be a mixture of titanate of iron with variable quantities of the oxide and sesquioxide of that metal. Rose and Scherer, however, believe it to be a mixture of the sesquioxides of titanium and iron.

Pure *titanic acid* is usually obtained from rutile or titanic iron. The ore is reduced to fine powder, and its iron oxides extracted with hydrochloric acid. The residue is then fused with carbonate of soda, and the resulting mass treated with water to dissolve excess of alkali. Acid titanate of soda remains, which is washed in a filter, until the liquid passes through cloudy. It is then removed from the filter, and dissolved in strong hydrochloric acid. The solution is diluted with water, charged with sulphuretted hydrogen, which throws down whatever tin may be contained in the mineral. This is separated by filtration, and the liquid poured in a flask, which is corked, after the addition of ammonia. A precipitate, consisting of titanic acid and the sulphurets of iron and manganese now falls. The sulphurets are separated from the acid by the addition of sulphurous acid, *in excess*, and the titanic acid which remains is thoroughly washed.

A simpler method of obtaining it is to ignite titanic iron with sulphur, so as to convert the iron into a sulphuret. The sulphuret of iron is removed by hydrochloric acid. By repeating the operation several times, the titanic acid may be obtained quite free from iron.

Titanic acid is a white, tasteless, infusible powder, which becomes yellow on the application of heat, but, like oxide of zinc, regains its whiteness as it cools. Like silicic acid, it occurs in two modifications, a soluble and an insoluble. Like it, too, the former is converted into the latter by ignition.

Ammonia precipitates it white, gelatinous, soluble in acids, and to some extent in carbonated alkalies. Ferrocyanide of

potassium throws down a reddish-brown precipitate, soluble in excess of the reagent; zinc, iron, and tin, added to its solutions, first change their color to a blue or purple hue, and then throw down a precipitate of the same tint, which gradually changes to titanic acid. This precipitate is supposed to be a sesquioxide of titanium.

For the purposes of the dentist, the purer varieties of the native acid are selected, and reduced to fine powder. As already stated, the presence of a small quantity of iron or manganese is not objectionable, as the tint is lowered by them, so as to approximate more nearly to the natural hue of the teeth. It is necessary, however, for the operator to know either the exact proportion of these metals present, or the precise color which any given specimen of titanium will yield. Trial pieces should, therefore, always be used, or the pure acid employed and the color deadened by other oxides.

OXIDE OF URANIUM.

Uranium was originally discovered by Klaproth in 1788, as an oxide, but Peligot was the first to obtain the metal, in 1841.

It is contained in considerable quantity in *uranite*, of which there are two varieties, both represented by the formula $3RO\,PO_5+2(3U_2O_3,PO_5)+24HO$. In one of these, *lime uranite*, the RO is CAO with a little BaO. In the other, *chalcolite* or copper uranite, it is CuO. Both varieties crystallize in the quadratic system, with many octahedra. The lustre of the end-plane is pearly, of the rest adamantine. Both are transparent or subtranslucent, sectile, and brittle. The color of *lime uranite* is yellow or greenish, that of *copper uranite* emerald and other bright greens with a paler streak. Both yield water when heated in a tube, becoming yellow as it is expelled. Both fuse on coal with effervescence to a black bead with a crystalline surface; dissolve in fluxes with a yellow color in the outer and a green in the inner flame, and form a yellow slag with soda. Chalcolite gives, besides these, the reactions of copper.

Uranium, or *pitchblende*, contains a still larger proportion of this metal. It occurs massive, is opaque, black, brownish or grayish in color, with a dull, submetallic lustre and a conchoidal

fracture. It is infusible alone, but with the fluxes it dissolves into a yellow glass in the outer and a green one in the inner flame. By the aid of heat, it dissolves in both nitric and nitro-muriatic acids.

It is found in many places in Europe. In the United States it has been found at Middletown, Connecticut; Chesterfield, Massachusetts; and Chester, Pennsylvania, on the Delaware River.

Uranium has three oxides. The first (UO) is a reddish-brown or iron gray powder. It forms green salts.

The second, or common oxide of uranium, is a mixture of the first and third, and is obtained in large quantities from uranium or pitchblende, which contains from 50 to 90% of it. The ore is dissolved in *aqua regia*, and charged with sulphuretted hydrogen, to remove other metals, and the solution filtered clear from the precipitate. The filtrate is heated with nitric acid to peroxidize the iron and uranium, which are then thrown down by ammonia. The precipitate is washed, and then treated with carbonate of ammonia, which dissolves the cobalt, zinc, nickel, and uranium. The ammonia is volatilized by heat, and the residue washed, dried, and ignited. Digestion with muriatic acid takes up the other oxides, and leaves the green oxide of uranium.

It is a dark green or black powder, soluble in concentrated hydrochloric or nitric acid, when digested with either in a close vessel; peroxidized by nitric acid, forming green salts with the acids, which dissolve it unchanged.

The *sesquioxide*, U_2O_3, is obtained by dissolving the green oxide in nitric acid, evaporating to dryness, and fusing it at a low heat to drive off nitric acid. It is then digested in boiling water as long as anything soluble is taken up, and the pure oxide remains as a gold or orange yellow powder, becoming brick red, from loss of water, by careful heating; and, at a higher temperature, losing oxygen also. Its salts are yellow. This is the oxide used by the manufacturer of porcelain teeth.

OXIDE OF MANGANESE.

The oxide of manganese occurs native in a variety of forms. It is sometimes mixed with lime, as in *manganese spar*, and *manganoealcite*, sometimes with silica, as in *Fowlerite*, *Troostite*, &c. Most commonly, however, it is found alone or only contaminated with iron and other accidental admixtures. *Manganite* is a crystallized form, containing one atom of water, in right rhombic, longitudinally striated prisms. It is most frequently met with, however, in black, earthy masses, which are always more or less impure.

There are no less than six different degrees of oxidation of this metal, the protoxide, MnO; the red oxide, Mn_3O_4, thought by some to be a mixture of the proto- and sesquioxides; the black or sesquioxide, Mn_2O_3; the binoxide, MnO_2; manganic acid, MnO_3, and permanganic acid, Mn_2O_7. Of these, the third and fourth only are used in tinting glass and porcelain.

There are various modes of obtaining the pure oxides from the commercial black oxides. One of the simplest and readiest of these, is to make an intimate mixture of the peroxide of commerce with half its weight of sal ammoniac, and to project it portionwise into a crucible kept constantly at a red heat. The chlorine of the salt, in this process, unites with the oxide of manganese, to the exclusion of every other substance, provided an excess of that oxide be present. The chloride of manganese is extracted from the mass by digestion in water. Another simple method is to mix the commercial oxide with sulphuric acid, to a paste, to introduce this into a crucible, heat it to redness for half an hour or an hour, and lixiviate. In either case, the sulphate or chloride is to be precipitated by an alkaline carbonate or a pure alkali, and then again heated to redness. Should the peroxide be required, the last-mentioned precipitate is to be dissolved in nitric acid, and the resulting nitrate decomposed by heating it to a commencing redness.

Oxide of zinc is obtained by simply burning the metal and collecting the fumes as they rise.

Oxide of silver has been described already.

OXIDE OF COBALT.

The ores of cobalt almost always contain nickel, iron, arsenic, and manganese. A variety of processes have been adopted for the separation of the pure oxide on the great scale. We shall only specify one method, that of Quesneville, by which a tolerably pure oxide can be obtained from the ore.

The ore is to be boiled in nitric acid, to convert the arsenic into an oxide, which combines with the different metals present. The solution is then largely diluted and filtered, and the arseniates are precipitated, one after another, by means of carbonate of soda. The arseniate of cobalt, which is the most soluble, precipitates last. The alkali is to be added in small quantities and at considerable intervals of time, the solution being frequently stirred, or otherwise agitated, and the precipitates obtained, after each addition of the alkali, being allowed to subside thoroughly from the clear solution. In this manner, the colors of the precipitates can be distinctly recognized. When a rose-colored precipitate begins to fall, no more alkali must be added, as this is an indication that cobalt is coming down. The solution is now filtered off from the precipitates, and the clear liquid precipitated by a saturated solution of binoxalate of potassa, which in a few hours throws down the cobalt, mixed with a little nickel. The latter oxide may be entirely separated from the cobalt, if desired, by bringing both of them to the condition of oxalates, dissolving the mixed salts in ammonia, and exposing to the air for several days, when the nickel falls, leaving cobalt in solution.

A preparation, called *ashes of cobalt*, said to be superior to the pure oxide as a coloring material for teeth, is made by wrapping the oxide in blue English laid paper, and burning it in a closed crucible.

In the production of the natural tints of the teeth and gums from these positive colors, much taste and skill are required. No general directions can be given which will meet the emergencies

of particular cases, for the tints of natural teeth are so varied, that the variations of the coloring matters to imitate them must be almost endless. The quantity of oxide introduced into the composition must be extremely small.

Linderer gives receipts for five different shades of yellow and of blue, and for six of the greenish tints. To 37 pennyweights of the dry materials of the teeth, he adds 2 grains of titanic acid for his palest and 8 for his deepest yellow; and $1\frac{1}{2}$ grains of platina sponge for his palest and 4 for his deepest blue. For his green tints, he mixes for No. 1, the palest, 3 grains of titanic acid with 1 of platina sponge, and for No. 6, the deepest, 8 grains of the former with 4 of the latter. These tints are for the bodies.

We shall return to this subject, after having described the method of manufacturing the porcelain teeth themselves.

CHAPTER VIII.

INCORRUPTIBLE TEETH.

HISTORY.

Numerous were the substitutes employed by the old dentists to replace teeth which had been unfortunately lost or removed from the mouth. Human teeth, the ivory of the elephant or hippopotamus, and such animal substances constituted their sole resources. These were objectionable not only on account of the imperfect manner in which they imitated the natural organs, but also by reason of their permeability to offensive fluids, the readiness with which they absorbed, and the tenacity with which they retained disagreeable effluvia.

It was to the discomfort of an apothecary of St. Germain, named Duchateau, that the world owes the beautiful and unchangeable material which is at present used in the fabrication of dental substitutes. This vender of drugs, having had the

misfortune to lose his teeth, had supplied the deficiency with one of the ivory imitations common in his day. Living, as he did, in an atmosphere perpetually tainted with the various disagreeable odors arising from his wares, he found that the porous animal substances of which his artificial teeth were composed, imbibed these effluvia, and became a perpetual source of discomfort to their wearer. Casting about in his own mind for a substitute for these uncleanly organs, he hit upon porcelain, which recommended itself strongly to him by its beauty, impermeability, and durability. M. Guerard undertook the manufacture of the articles, and the first set of porcelain teeth saw the light in Paris, in 1776, a year famed for a more memorable revolution.

Encouraged by his success, he prevailed on others who were in the same unpleasant predicament with himself to resort to the same expedient for relief. He had several complete dentures made for different distinguished personages, but he failed for want of knowledge of the practical duties of the dentist, and for some time these substitutes were abandoned.

After a time, one Dubois Chement (in 1788) purchased the right of Duchateau, and made great efforts to establish these substitutes in the confidence of the public. He succeeded in attracting the attention of the French Academy, who appointed a committee to examine his process. It was found to be defective in many respects, and Dubois-Foucou, who was one of the committee, set to work to improve it. At last he succeeded in getting out a material which, with some modifications, serves as the basis of our present processes.

It is not necessary to trace our history farther. Suffice it to say, that his process has been greatly improved since those days, and that our own country has not been behind others in its contributions to the advancement of this beautiful art.

PREPARATION OF MATERIALS.

In all operations in which a perfect fusion is required, it is essential that the substances to be fused should be reduced to a state of the completest possible comminution, and mixed in the most intimate possible manner. The semivitrification of

porcelain needs the same fine pulverization and perfect admixture, for it is a true fusion.

Great care is therefore taken to comminute the materials as completely as possible. The silex is first heated to redness, and then suddenly quenched in water. This makes it friable, and very much facilitates its subsequent reduction. Some prefer to grind up the coloring matter along with the silex. The grinding is usually accomplished in porcelain or wedgewood mortars, and the mass is commonly kept constantly moist. This answers two good purposes: it prevents the fine particles from rising in the air, and it facilitates the comminution of the substances. The spar is treated in the same manner, or it may be powdered without any preparatory ignition. The kaolin is directly powdered.

It is sometimes necessary to purify this latter ingredient, as few specimens, however fine, are totally free from iron. All that is necessary is to digest it with dilute hydrochloric acid, and afterwards to wash it thoroughly. Iron is injurious to the porcelain in more ways than one. It not only gives an unpleasant yellow opacity to the wares, but it also so increases the fusibility of the compound as to render it impossible to calculate upon its fusing point.

It is customary with some manufacturers to reduce their silex to a much finer powder than their spar. They think that they thereby increase its transparency. Some go so far as to make this powder very coarse, but we doubt the propriety of such a mode of procedure. It is the fusible portion which they treat in this manner, and the only effect it can have is to retard the melting of the spar. Were the silex left coarse, or were a few fragments additional of this substance, or of asbestos, introduced into the body, it would, like the cement in a crucible, materially diminish contraction.

The extreme comminution, perfect intermixture, and absolute purity of the materials, is especially to be insisted on in the preparation of the enamel. Any defect becomes very manifest. Grains of unfused silex roughen the surface, which ought to be perfectly smooth, or spots and stains disfigure it. The process of grinding the substances thoroughly, then stirring them with

a large quantity of water, allowing the coarser particles to subside, and decanting the finer powder, may be resorted to with advantage. Audibran used a porphyry slab and muller for levigating the materials he designed to use. When the materials are ground under water, they may be rapidly dried by throwing the paste upon some clean porous substance, such as a well-dried slab of plaster of Paris, till so much water is abstracted from it as to leave it of the consistence of stiff dough.

Several little circumstances must be attended to by the manufacturer who would obtain perfect teeth. Many of these can only be learned by experience, so that it is impossible to give general directions which shall apply to individual cases. A few general principles, however, may be stated, which will serve as a guide to the operator. The practical details must in this, as in all other cases, be determined by the skill and tact of the manipulator. It is necessary, in the first place, to use pure water, rain water is best, so as to avoid contaminations of coloring matters and of salts, the latter of which will increase the fusibility of the pastes. It is proper, also, to let the kaolin moulder, as we have already described under the head of porcelain. The contraction in the furnace to which we have already alluded in a previous chapter, must also be borne in mind. Audibran recommends to make all the teeth and blocks one-third larger than they are designed to be after baking.

The fusibility of the enamel is another important point. If it is too thin, it will sink into the body and yield a most imperfect glaze; if too glassy, it will overstep the modesty of nature; if too stiff, it will not fuse sufficiently. The heat must also be carefully regulated. If it be too high, the coloring matters do not produce their full effect, indeed many of them lose their tints when very intensely heated. This is one explanation of a fact, familiar to every practical man, that the same combinations do by no means always furnish the same results.

The color of the body must always harmonize with that of the enamel. It is improper to make body without coloring matter, for all teeth, which are perfectly healthy, possess a creamy or slightly yellow tint, belonging to the dentine, which is seen through the enamel, and this must be imitated as closely

as possible by the manufacturer of artificial teeth; and he can only do it by coloring the body, and then spreading a suitably tinted enamel over it.

The mechanical processes of making a *matrix*, *moulding* and *carving* artificial teeth do not properly belong to a treatise like this. They are already described by Dr. Harris, in his *Principles and Practice of Dental Surgery*, to which we refer the reader.

Crucing or Biscuiting.—In regard to this process, we have little to add to what we have already said in the chapter on porcelain.

After drying, the blocks are subjected to a full red heat, so as to agglutinate the particles without fusing the paste. This may be done either in an open charcoal fire, or in a muffle. The latter is commonly preferred, and the proper time to withdraw them is known by the condition of test pieces, which are examined from time to time. When these have become so dense that they may be scratched with a knife with some little difficulty, the crucing is complete.

Any defects in the form of the teeth are now corrected by filing and dressing up. The platinum pins are also introduced by drilling holes in the teeth, and packing a thin batter of paste around the metal, after the biscuited blocks have been first immersed in water.

Enamelling.—After the blocks are cruced, the enamel is applied with a camel-hair pencil. It must be of the consistence of thin paste or cream, and it must be applied so as to extend a little beyond the edge of the incisors and cuspidati, in order to obtain the translucency of the natural organs.

Sometimes only two, but oftener three, different colors of enamel are spread upon the biscuit, which must first be thoroughly cleaned. These tints are a grayish-blue for the lower part of the crowns, a yellowish for the portion nearer the gums, and a rose red for the gums. The red is applied first, then the yellow, and lastly the gray. The first tint should have a sharply defined margin, but the other two should be blended, so that they may fade into one another.

Firing and Baking.—We have already described and figured the furnace for baking teeth. (See page 252.) We have now

only to speak of the method of using it. The fire must be clear and strong. Anthracite is usually preferred as fuel. The fire is kindled with charcoal, and after it is fully ignited, the anthracite is added in portions till the furnace is full. The coal, when thoroughly ignited, should be two or three inches deep on the top of the muffle.

All the openings of the furnace are closed and luted after the slide has been introduced into the muffle. When the baking is complete, the door of the muffle is opened, and the slide partially withdrawn. This point is known by the fusion of the enamel. As soon as this has run evenly over the teeth, the process has been carried far enough. The work is allowed to remain until the slide is cool enough to be handled. If this annealing, or gradual cooling process should be neglected, the teeth will be apt to split and fly before the blowpipe.

Composition and Preparation of Body.—The formulæ for the body of artificial teeth are almost endless. Every one varies them according to his own notions or the results of his individual experience. We shall not multiply recipes, therefore, but confine ourselves to a very few.

No. 1.

Delaware spar	12 oz.
Silex	2 oz. 8 dwt.
Kaolin	7½ dwt.
Titanium	18 to 36 grs.

No. 2.

Delaware spar	16 oz.
Silex	3½ oz.
Kaolin	½ oz.
Titanium	20 to 60 grs.

"Put the titanium in a large mortar, and grind until it is reduced to an impalpable powder; then add the silex, and grind from one to three hours, or until there shall be no perceptible grit; now add the kaolin, and grind from thirty minutes to an

hour and a half; and, lastly, add the spar, little by little, and grind from forty to sixty minutes."*

No. 3.

Spar	12 oz.
Quartz	3 "
Kaolin	1 "

Oxide of titanium, 12 to 18 grains, in proportion to the depth of color desired.

No. 4.

Spar	40 oz.
Quartz	8 "
Kaolin	5 "

Oxide of titanium, 40 to 60 grains.†

For the above formulæ, I am indebted to Dr. A. A. Blandy, Professor of Operative Dentistry in the Baltimore College of Dental Surgery; and I am assured by him that they are those commonly used by him in the manufacture of artificial teeth, and that they have always been successful in his hands. I am also indebted to him for all the other formulæ in this chapter not otherwise credited.

Colors.—Coloring matters vary very greatly in the intensity of their dyeing power. Delabarre gives the following table of oxides, arranged according to the depth of tint which they impart to enamels, and it may be consulted with advantage by all engaged in the manufacture of incorruptible teeth:—

TABLE.

For 4 grammes are required			to color
Of cobalt,	0.0000535	grammes,	blue.
" platinum,	6.0000535	"	grayish-blue.
" gold,	0.0013400	"	violet and red.
" bismuth,	0.0026800	"	bluish-gray.
" mercury,	0.0026800	"	gray.
" silver,	0.0026800	"	pale yellow.

* Harris, Principles and Practice of Dental Surgery.

† Gum body, it must be observed, is made up without titanium.

Of iron,	0.0066900	grammes,	yellowish-red.
" manganese,	0.0138000	"	gray.
" uranium,	0.0535000	"	straw yellow.
" titanium,	0.1070000	"	"
" antimony,	0.2140000	"	yellow.

It is customary to reduce these oxides by previous fritting. This is accomplished by mixing them intimately with some fusible silicate, and subjecting them to sufficient heat to agglomerate them perfectly, and to vitrify them upon the surface. It is, in fact, a semivitrifaction.

The special frits will now be described.

Blue Frit.—Mix intimately, after powdering very finely, 4 dwt. of platina sponge with $\frac{1}{2}$ an ounce of spar (Boston spar is recommended, on account of its greater fusibility). Grind very fine, and frit by making up into a ball with water, and fusing very slightly upon a tile. While still hot, plunge it into water, and, when dry, pulverize it very minutely.

Yellow Frit.—Mix very intimately 2 dwt. of oxide of titanium with $\frac{1}{2}$ an ounce of spar, and heat it as before.

Gum Frit.—Purple of Cassius,* 8 grains; flux, 87 grains; spar, 350 grains. The purple of Cassius is first to be reduced to a very fine powder; the flux then added, by small portions at a time; the mass being continually ground, to secure fine comminution and perfect intermixture. The spar is now to be added, also portionwise, and the grinding continued till the whole is reduced to an impalpable powder.

This is now to be placed in a clean white Hessian or French crucible, lined with kaolin or powdered rock crystal, made into a paste with a little water. A cover is luted on to prevent ashes, cinder, or smoke, from contaminating the contents. Heat is then to be applied, sufficient to fuse the mixture. This fusion should not run on to perfect vitrifaction; for, if the flux be too thin, the gold will sink through it, and collect as a metallic button at the bottom. The fusion being completed, the frit is removed, and all foreign matter carefully separated from it. It

* That made by fusing gold, tin, and silver, and dissolving out the silver with nitric acid, is the proper purple for this process.

is then pulverized so finely as to pass through a No. 9 bolting-cloth.

Another *gum frit* is given by Dr. Harris, composed as follows: Metallic gold, in a state of minute division, 16 grains; flux, 175 grains; spar, 700 grains. Treat as before.

The *flux* alluded to above is composed of silex, 4 ounces; glass of borax, 4 ounces; salt of tartar, the common carbonate of potash, 1 ounce.

These ingredients are well pulverized and intimately mixed. They are then introduced into a perfectly white Hessian crucible, which is to be covered with a tile or a smaller crucible, well luted on, and subjected to a heat sufficient to fuse the contents perfectly. When this is properly done, the result is a beautifully transparent glass, free from any tint or stain whatever. This is to be reduced to a fine powder, and put away in a closely stoppered bottle for use.

Gold Mixture.—This preparation, which is also called *silicate of gold*, is made by dissolving 8 grains of pure gold in aqua regia, and stirring into the solution 15 dwts. of spar. As soon as it is sufficiently dry, make it into a ball, and frit it gently on a tile. Especial care must be taken not to fuse this preparation thinly, or the gold will melt and sink through the flux, destroying the coloring matter. The frit, thus prepared, is then to be reduced to powder, and set aside for use.

This preparation is used for lowering the tone of the titanium frits, which, without it, would give too brilliant and decided a yellow to the enamel.

Enamels.—These are more fusible than the body, and must be so composed that they will flow evenly over the biscuit during the baking of the teeth. Their colors must, of course, vary very greatly, and the skill of the manufacturer is shown in the proper management of his coloring materials to produce the infinite variety of tints which we see in nature. It is therefore manifest that no absolute formulæ can be given. The best is but the expression of that composition which is applicable to the greater number of cases.

Grayish-Blue Enamel.

No. 1.

Spar	1 oz.
Blue frit	5 grs.

No. 2.

Boston spar	2 oz.
Platina sponge	¼ gr.
Oxide of gold	½ "

No. 3.

Boston spar	2 oz.
Platina sponge	½ gr.
Oxide of gold	½ "

No. 4.

Spar	2 oz.
Platina sponge	¾ gr.
Oxide of gold	½ "

Yellow Enamel.

No. 1.

Spar	1 oz.
Yellow frit	4 grs.
Gold mixture	20 "

No. 2.

Boston spar	2 oz.
Titanium	10 grs.
Platina sponge	½ gr.
Oxide of gold	½ "

No. 3.

Boston spar	2 oz.
Titanium	14 grs.
Platina sponge	½ gr.
Oxide of gold	½ "

No. 4.

Boston spar	2 oz.
Titanium	10 grs.
Platina sponge	½ gr.
Oxide of gold	½ "

Of the above recipes, the two marked No. 1 were furnished me by Dr. A. A. Blandy, who has used them extensively, and found them to yield excellent results in practice. The rest are taken from the work of Dr. Harris, who observes: "No. 2 of the blue, and No. 4 of the yellow, will produce an enamel which will suit a larger proportion of cases than almost any other. The coloring ingredients should be ground fine, with five or six dwts. of the spar, when the remainder of the spar should be added, a little at a time, and ground from thirty to forty minutes."

Gum Enamel.—It is customary, in the preparation of this enamel, to grind the spar rather coarsely, that it may communicate a granular appearance to the enamel after fusion. The quantity of frit necessary to produce the proper effect must be learned by experience. As this varies in its coloring power, in accordance with the varying nature of the purple of Cassius, which constitutes its basis, to which reference has already been made, many dentists mix varying proportions of frit and spar, and bake them on different pieces of biscuit, so to feel, as it were, for the desired hue.

A formula, which has been found to furnish an excellent color, is:—

Gum frit	30 grs.
Spar	4 dwt.

In this matter of gum color, there is great room for the display of individual skill. The hues of the natural gum are very various. Some gums are very florid; others very pale; some nearly purple; some almost white. Many gums are paler just over the ridges of the alveoli and the fangs of the teeth. Some have a yellowish suffusion over their basis of rose-color. All these varieties must be imitated by the skilful manufacturer,

and there is but one method to acquire the necessary skill. The behavior of the oxides must be carefully studied, and a thorough understanding of the effects of their admixture must be acquired.

Dr. Hunter has introduced a new method of manufacturing these dental substitutes, and, not to do him injustice by an abridgment, his own account of the process is copied from his paper in the *American Journal of Dental Science* for October, 1852.

"*Silex* should be of the finest and clearest description, and kept on hand ready ground, the finer the better.

"*Fused Spar* should be the clearest feldspar, such as is used by tooth manufacturers for enamels, completely fused in a porcelain furnace, and ground fine.

"*Calcined Borax* is prepared by driving off the water of crystallization from the borax of commerce, by heating in a covered iron vessel over a slow fire, and it is better to use immediately after its preparation, as it attracts moisture. It should be perfectly clean and white, and free from lumps.

"*Caustic Potassa.*—Known also as potassa fusa.

"*Asbestos.*—Take the ordinary clean asbestos, free it from all fragments of talc or other foreign substances, and grind fine, taking care to remove any hard fragments that may occur.

"*Granulated Body.*—Take any hard tooth material (I use the following formula: spar 3 oz., silex 1½ oz., kaolin ½ oz.), and fuse completely. Any very hard porcelain, wedgewood ware, or fine china, will answer the same purpose. Break and grind so that it will pass through a wire sieve No. 50, and again sift off the fine particles which will pass through No. 10 bolting-cloth. It is then in grains about as fine as the finest gunpowder.

"*Flux.*—Upon this depends the whole of the future operations, and too much care cannot be taken in its preparation. It is composed of silex 8 oz., calcined borax 4 oz., caustic potassa 1 oz. Grind the potassa fine in a wedgewood mortar, gradually add the other materials until they are thoroughly incorporated. Line a Hessian crucible (as white as can be got) with pure kaolin, fill with the mass, and lute on a cover, a piece of fire-clay slab, with the same. Expose to a clear strong fire in a furnace with coke fuel, for about half an hour, or until it

is fused into a transparent glass, which should be clear and free from stain of any kind, more especially when it is to be used for gum enamels. Break this down and grind until fine enough to pass through a bolting-cloth, when it will be ready for use.

"*Base.*—Take flux 1 oz., asbestos 2 oz., grind together very fine, completely intermixing. Add granulated body 1½ oz., and mix with a spatula to prevent grinding the granules of body any finer.

"*Gum Enamels.*—No. 1. Flux 1 oz., fused spar 1 oz., English rose 40 grains. Grind the English rose extremely fine in a wedgewood mortar, and gradually add the flux, and then the fused spar, grinding until the ingredients are thoroughly incorporated. Cut down a large Hessian crucible so that it will slide into the muffle of a furnace, line with silex and kaolin each one part, put in the material, and draw up the heat on it in a muffle to the point of *vitrifaction*, not *fusion*, and withdraw from the muffle. The result will be a red cake of enamel which will easily leave the crucible, which, after removing any adhering kaolin, is to be broken down and ground tolerably fine. It may now be tested, and then (if of too strong a color) tempered by the addition of covering. This is the gum which flows at the lowest heat, and is never used when it is expected to solder.

"No. 2. Flux 1 oz., fused spar 2 oz., English rose 60 grains. Treat the same as No. 1. This is a gum intermediate, and is used upon platina plates.

"No. 3. Flux 1 oz., fused spar 3 oz., English rose 80 grains. Treat as the above. This gum is used in making pieces intended to be soldered on, either in full arches or in the sections known as *block-work*. It is not necessary to grind very fine in preparing the above formulæ for application.

"*Covering.*—What is termed covering, is the same as the formulæ for gum, *minus* the English rose, and is made without any coloring whatever when it is used for tempering the above gums which are too highly colored, and which may be done by adding, according to circumstances, from 1 part of covering to 2 of gum, to 3 of covering to 1 of gum, thus procuring the desired shade. When it is to be used for covering the base prior to applying

the gum, it may be colored with titanium, using from two to five grains to the ounce.

"*Investient.*—Take two measures of white quartz sand, mix with one measure of plaster of Paris, mixing with just enough water to make the mass plastic, and apply quickly. The slab on which the piece is set should be saturated with water to keep the material from setting too soon, and that it may unite with it.

"*Cement.*—Wax 1 oz., rosin 2 oz. The proportion of this will vary according to the weather; it should be strong enough to hold the teeth firmly, and yet brittle enough to chip away freely when cold. A little experience will enable any one to prepare it properly.

"Platina, as usually applied, I think objectionable, wanting stiffness; my method of using it is similar to that proposed by Delabarre, but possessing greater strength than even his method, and by it can be made as light as a good gold plate got up in the ordinary way. I first strike a very thin plate to the cast, and cut out a piece the size of the desired chamber, taking care not to extend it forward to embrace the palatine artery. Add wax to the plate for the depth of cavity, diminishing it neatly as it approaches the alveolar ridge. Cement this plate to the cast and take another metallic cast, strike another thin plate over the whole, and solder throughout with an alloy, of gold twenty-two parts, platina two parts, or with pure gold. The chamber thus formed is precisely the same as 'Cleveland's Patent Plate,' but the space *between the plates*, for which he obtained his patent, is subsequently filled up, leaving a cavity resembling Gilbert's, but with a sharper edge when so desired. This space is filled up with base and enamel, and gives greater stiffness without the ugly protrusion of the struck chamber. The plate thus formed assimilates much more closely to the palatal dome, not interfering with pronunciation; another great advantage gained by it is the impossibility of warping. I say *impossibility*, because I have submitted plates so constructed to the severest tests, and never had them to warp. It is well to rivet the two plates together before proceeding to solder, especially gold plates, and to bring the heat carefully upon them; once prepared there is no danger of change in the succeeding manipu-

lations. I strike up the lower plate with a band on the labial edge about one-sixteenth of an inch wide. This I do by trimming the wax impression before taking the plaster cast, or by building a ridge of wax on the plaster cast before taking the metal casts. Should the band (or turned edge) flare out too much, it may readily be bent in with a pair of pliers, &c. This style of work should not be applied except where the absorption may be said to be complete.

"After the plates are perfectly adapted to the mouth, place wax upon each, which trim to the proper outline as regards length and contour of countenance, marking the proper occlusion of the jaws and the median line. These waxen outlines are called the *drafts*, and are carefully removed from the mouth, and an articulator taken by which to arrange the teeth.

"When the absorption is considerable, and the plate in consequence is rather flat, it is necessary to solder a band or rim along the line where the upper draft meets the plate, about one sixteenth or one-eighth of an inch wide, and fitting up against the outline of the draft. When the ridge is still prominent, the block will not of course be brought out against the lip so much, and a wire may be soldered on instead of the wider band. I think one or the other necessary, as it gives a thick edge to the block, rendering it far less liable to crack off than if it were reduced to a sharp angle; it also allows the edge of the plate to be bent in against the gum, or away from it, as circumstances may require, and afford, in many cases, a far better support for the plates than can be given to one in which the band is *struck up*, or the edge turned over with pliers, where the block must extend to the edge of the plate. Some few cases do occur, when the band may be struck as far back as the bicuspids with advantage, and some in the lower jaw where it is necessary to solder on the band, but the general practice is not so.

"The upper teeth are first arranged on the plate antagonizing with the lower draft, supported by wax or cement, or both. Then remove the lower draft, and arrange the lower teeth, so that the coaptation of the cutting edges of the teeth shall be perfect as desired. The patient may now be called in again, and any change in the arrangement made to gratify his or her

taste or whim. Now place the plate, with the teeth thereon, on their respective casts, oil the cast below the plate, and apply plaster of Paris over the edge and face of the teeth and down on the cast, say an inch below the edge of the plate. This will hold them firmly in their place while you remove the wax and cement from the inside, and fit and rivet backs to the teeth. When backed, cut the plaster through in two or more places, and remove. Clean the plate by heating. Cut the plaster so that, while it will enable you to give each tooth its proper position, you can readily remove it from the teeth when they are cemented to the plate. Adjust the sections of plaster and the teeth in their proper positions. The plaster may be held by a piece of soft wire. *Cement* the teeth to the plate, and strengthen the cement by laying slips of wood half an inch long along the joint and against the teeth. (I generally use the matches which are so plenty about the laboratory.) Remove the sections of plaster, being careful not to displace any of the teeth. If it be intended to cover the strap with enamel, you should solder a wire, after backing, and previous to replacing the teeth, along the plate parallel with the bottom of the straps, and about an eighth or a quarter of an inch from them.

"The teeth are now backed and cemented to the plate, and present an open space between the plate and the teeth, which is to be filled up with the base, using it quite wet to fill up the small interstices, filling in the rest as *hard and dry as possible*. Fill the cavity *between* the plates in the same manner, and oil the edge. Oil the surface of the base, envelop in the investient (precisely as you would put an ordinary job into plaster and sand for soldering), and set on a fire-clay slab previously saturated with water. When hard, chip away the cement, cooling it if necessary with ice, until it is perfectly clean. Along the joints place scraps and filings of platina very freely, and cover all the surface you wish to enamel with coarse filings, holding them to their place by borax ground fine with water. Apply pure gold as a solder quite freely, say two dwt. or more to a single set. Put in a muffle, and bring up a gradual heat until the gold flows *freely*, which heat is all that will be needed for the base; withdraw, and cool in a muffle. Remove the investient and fill up

all crevices and interstices not already filled, with covering No. 2; cover the straps and base with the same, about as thick as a dime, and cover this with gum No. 2, about half that thickness. At the same time enamel the base in the chamber, and cover with thick soft paper. Set the plate down on the investient on a slab, with the edges of the teeth up. Fuse in a muffle, and the work is completed. Blemishes may occur in the gum from a want of skill in the manipulation; should such occur, remedy by applying gum No. 1.

"Should the patient object to the use of platina as a base, the work can be made as above on an alloy of gold and platina 20 carats fine, and soldered with pure gold, &c. as above. In all cases, however, where it is used, the upper plate should be made as I have described above, but with platina any kind of plate can be used.

"*Ordinary Alloy.*—Blocks may be made and soldered to the ordinary plate if the absorption is sufficient to require much gum, without any platina. Arrange the teeth on wax on the plate, fill out the desired outline of gum, and apply plaster a quarter of an inch thick over the face of teeth, wax and cast. When hard, cut it into sections (cutting between the canines and bicuspids), remove the wax from the plate and teeth, bind the sections of the plaster mould thus made to their places with a wire, oil its surface and that of the plate, fill in the space beneath the teeth with the base, wet at first, but towards the last as hard and dry as possible, and thoroughly compacted. Trim to the desired outline on the inside, oil the base, and fill the whole palatal space with investient, supporting the block on its lingual side. Remove the plaster mould and cut through the block with a very thin blade between the canines and bicuspids. Take the whole job off of the plate, and set on a fire-clay slab with investient, the edges of the teeth down; bring up the heat in a muffle to the melting point of pure gold. When cold, cover and gum with No. 3 gum and covering.

"Another mode is to back the sections with a continuous strap (using only the lower pin), fill in the base from the front, use covering and gum No. 3, and finish at one heat. When the blocks are placed upon the plate, the other pin is used to fasten

the gold back, which is soldered to it, and the platina half-back; neither of these backs need be very heavy, as soldering the two together gives great strength and stiffness. Very delicate block-work can be made in this way, and it is applicable also where a few teeth only are needed.

"A very pretty method, where a section of two or four teeth (incisors) is needed and only a thin flange of gum, is to fit gum teeth into the space, unite by the lower platina with a continuous back, and unite the joint with gum No. 3. A tooth left ungummed by the manufacturer would be best for the purpose. The same may be applied to blocks for a full arch, remembering not to depend entirely upon platina backs.

"The method I prefer for full arches on ordinary plate, is to take a ribbon of platina a little wider than the intended base, and of the length of the arch, cut it nearly through in five places, viz. between the front incisors, between the lateral incisors and canines, and between the bicuspids. Adapt it to the form of the alveolar ridge with a hammer and pliers, and swage on the plate along where the teeth are to be set. Solder up the joints with pure gold, and proceed to back the teeth, &c., as before; making preparations for fastening, and removing the slip of platina from the gold plate before enveloping in the investient, when proceed as before.

"When the teeth are arranged, insert four platina tubes about one line in diameter, two between the molars, and two between the cuspidati and bicuspids, and solder to the platina base. These are designed, after the teeth are finished, to be the means of fastening to the gold plate, either by riveting in the usual way, or by soldering pins to the gold plate passing up through the tubes, fastening with sulphur or wooden dowels. By these methods we are enabled to readily remove the block and repair it, should it meet with any accident, and also, in case absorption should go on, to restrike the plate, or to lengthen the teeth. The rim should be put on the gold plate after the block is finished; it gives great additional strength and a beautiful finish.

"*Memoranda.*—In preparing material, always grind dry, and the most scrupulous cleanliness should attend all the manipulations. In all cases where heat is applied to an article in this

system, it should be raised gradually from the bottom of the muffle and never run into a heat. Where it is desired to lengthen any of the teeth, either incisors or masticators, or to mend a broken tooth, it may be done with *covering*, properly colored with platina, cobalt, or titanium.

"In repairing a piece of work, wash it with great care, using a stiff brush and pulverized pumice-stone. Bake over a slow fire to expel all moisture, and wash again, when it will be ready for any new application of the enamel. Absorption, occurring after a case has been some time worn, by allowing the jaws to close nearer, causes the lower jaw to come forward and drive the upper set out of the mouth. By putting the covering on the grinding surface of the back teeth in sufficient quantities to make up the desired length, the coaptation of the denture will be restored, and with it the original usefulness.

"Any alloy containing copper or silver should not be used for solder or plate, if it is intended to fuse a gum over the lingual side of the teeth, as it will surely stain the gum. Simple platina backs, alone, do not possess the requisite stiffness, and should always be covered on platina with the enamel, and on gold with another gold back. In backing the teeth, lap the backs or neatly join them up as far as the lower pin in the tooth, and higher, if admissible, and in soldering be sure to have the joint so made *perfectly soldered*.

"As the work on platina plate presents fewer difficulties to the tyro, it would be well to gain experience upon that kind of work before attempting its application to gold bases. The proper tooth for this work is not yet in the market, but I think will be ere long. A tooth finished at one heat by the manufacturer is best, although any tooth may be used that has been painted at a higher heat than the melting point of gold, being careful not to use any tooth in which gold may have been incorporated, as it will change color in the fire. A tooth with a natural shaped crown, but thinner than the natural tooth, with the platina pins at a point that will allow of the back being covered without being clumsy, is wanted, and likewise a tooth resembling the natural tooth, except that the molars be made with one conical fang similar to a dens sapientiæ."

Dr. Allen's formulæ are as follows:—

For the Base.—Silex, 2 ounces; flint glass, 1 ounce; borax, 1 ounce; wedgewood, $1\frac{1}{2}$ ounce; asbestos, 2 drachms; feldspar, 2 drachms; kaolin, 1 drachm; intermixed or underlined with scraps of gold or platina.

For the Enamel.—Feldspar, $\frac{1}{2}$ an ounce; white glass, 1 ounce; oxide of gold, $\frac{1}{8}$ grain. The latter ingredient gives the gum color.

INDEX.

*** Those words printed in SMALL CAPITALS indicate the heads of chapters.

A.

Acetic acid, 76
Acid, acetic, 76
  auric, 306
  benzoic, 80
  butyric, 77
  caproic, 78
  caprylic, 79
  carbazotic. (See Picric.)
  choleic, 73
  cholic, 85
  conjugated, 67
  cupric, 375
  döeglic, 85
  eläidic, 84
  formic, 76
  glycocholic, 71
  hippuric, 67
  hydrochloric, 121
  hydrofluosilicic, 463
  inosic, 71
  lactic, 81
  leucic, 57
  lithofellic, 85
  margaric, 83
  metacetonic, 77
  œnanthylic, 79
  oleic, 84
  osmic, 418
  oxalic, 75
  picric, 67
  propionic. (See Metacetonic.)
  sebacic, 80
  silicic, 451
  stearic, 91
  taurocholic, 72
  titanic, 480
  uric, 68
  urobenzoic. (See Hippuric.)
  valerianic, 78
Acids generated in indigestion, 131
Adularia, 471
Albite, 472
Albumen, change of, during digestion, 130
  coagulated, 35
  combinations of, 34
  composition of, 36
  preparation of, 36
  quantitative estimation of, 37
  soluble, 34
  tests for, 36
  varieties of, 33
  vegetable, 28
Albuminate of soda, 35
Albuminose, 130
ALBUMINOUS GROUP of animal substances, 28
Alcohol as fuel, 261
Aldehydes, 73
Allantoine, 63
Allen's formulæ for artificial teeth, 506
Alumina, 455
  a constituent of the body, 21
  silicates of, 457
  sulphate of, 456
ALUMINUM, 454
  chloride of, 456
Amalgamation of gold, 282
  silver, 325
Amalgam question, 441
Amalgams for mirrors, 401
  teeth, 444
Amides, 74
Ammones, 88
Ammonia, constitution of, 88
Anatase, 481
Aniline, 53
Anthracite, 266
Arsenic, 21

B.

Baking teeth, 491
Bell metal, 377
Benzoic acid, 80
relations to hippuric acid, 68
Bile, 132
chemical composition of, 133
influence on digestion, 141
metamorphosis of, in intestines, 147
morbid changes of, 134
origin of, 136
pigment, 102
quantity of, 135
relation of, to obesity, 130
respiration, 136
Bilifulvin, 103
Bilin, 72
Biliphæin, 103
Biliverdin, 103
Biscuit, 473
Bismuth, 412
alloys of, 414
bromide of, 415
chloride of, 415
iodide of, 415
metallic, 412
metallurgy of, 412
nitrate of, 416
oxides of, 413
phosphate of, 416
phosphuret of, 414
sulphate of, 415
sulphuret of, 414
Blowpipe, 237
Black's, 239
Cronstedt's, 237
directions for using, 244
Elliott's, 246
flame of, 243
Gahn's, 239
material for, 240
Mitscherlich's, 239
Parmly's, 245
self-acting, 245
table, 247
Wollaston's, 238
Body, composition and preparation of, 492
Hunter's, 499
Borax, 465
glass of, 465
Brass, 378
solder, 378
Britannia metal, 401
Bronze, 376
Brookite, 481
Butyral, 73
Butyric acid, 77
physiological relations of, 78
Butyrone, 74

C.

Calcium a constituent of the body, 19
Calculi, biliary, 135
formation of, 135
Calomel stools, 151
Cannon metal, 377
Caproic acid, 78
Caprylic acid, 79
Carats, 299
Carbazotic acid. (See Picric Acid.)
Carbon an element of the body, 19
Casein, coagulation of, 44
composition of, 45
digestibility of, 130
physiological relations of, 46
preparation of, 46
quantitative analysis of, 46
soluble, 43
tests of, 46
vegetable, 28
Cassius, purple of, 307
Cement, Willis's, 261
Cementum, analysis of, 154
Chalcolite, 483
Charcoal, peat, 269
wood, 267
Chlorine a constituent of the body, 19
Choleic acid, 73
Cholepyrrhin, 102
Cholesterin, 95, 133, 135, 140
Cholic acid, 85
formed from fat, 86
tests for, 86
Chondrin, composition of, 52
physiological relations of, 53
preparation of, 53
Chylopoine, 142
Clays, analysis of, 467
classification of, 468
composition of, 469, 470
distribution of, 466
effect of heat on, 468
for Hessian crucibles, 255
impurities of, 468
modes of increasing the pliancy of, 476
origin of, 466
refractory, 254
Coal, bituminous, 266
chemical composition of, 266

Coal, geological situation of, 265
mineral, 265
varieties of, 265
Cobalt, oxide of, 486
Coinage, gold, table of, 316
silver, table of, 347
Coke, 269
Conjugated acids, 67
Copper, 363
acetates of, 386
a component of the body, 21
alloys of, 376
metallurgy of, 369
ammonio-chloride of, 381
arsenites of, 386
black oxide of, 373
salts of, 383
borate of, 386
bromide of, 381
carbonate of, 385
chlorides of, 379
dioxide of, 372
salts of, 382
fluoride of, 381
hydruret of, 376
hyposulphate of, 384
iodide of, 381
metallic, 371
nitrate of, 385
nitruret of, 376
ores of, 364
dry assay of, 366
metallurgy of, 365
oxides of, 372
peroxide of, 375
phosphate of, 385
phosphuret of, 376
silicate of, 386
sulphate of, 383
sulphurets of, 375
Creatine, 54
Creatinine, 55
Crucibles, 254
Anstey's, 258
Beaufaye's, 258
black-lead, 258
characters of good, 256
clay, 258
composition of, 257
examination of, 257
Hessian, 258
iron, 258
London, 258
platinum, 259
porcelain, 258
silver, 258
Crucing, 491
Cupellation of gold, 282
silver, 330
on the large scale, 383
Cupels, 259
Cupric acid, 375

D.

Dentine, analysis of, 154
Digestion, 105
accelerated by fat, 139
diminished by acids, &c., 139
gastric, 119
influence of nervous system on, 129
intestinal, 132
Döeglic acid, 85
Drivelling, 197

E.

Eläidic acid, 84
Elements, proximate, of the body, 18
ultimate, 17
Enamel, analysis of the, 154, 155
artificial, formulæ for, 496
Enamelling, 491
Extractive matters, 104

F.

Fat, metamorphosed in liver, 139
origin of, 92
relations to bile, 138
muscular activity, 92
nutrition, 138
respiration, 93
sexual functions, 92
uses of, 93, 144
Fæces after iron, 151
after mercury, 151
chemistry of, 149
of infants, 151
Feldspar, 470
common, 472
glassy, 471
soda, 472
Fibrin, boiled, 39
coagulated, 37
composition of, 39
muscular. (See Syntonin.)
physiological relations of, 41
preparation of, 40
relations to tissue, 41
spontaneously coagulated, 37
tests for, 40
vegetable, 28
Fire-lute, Faraday's, 260

Fire-lute, Parker's, 260
Watts's, 260
Flame, oxidating, 243
reducing, 243
structure of, 241
Fluorine a constituent of the body, 20
Food, albuminous, 112
comparative value of vegetable and animal, 115
deficiency of, 117
gelatinous, 112
oleaginous, 112
Prout's classification of, 111
respiratory, 113
value of different articles as, 115
saccharine, 112
Formic acid, 76
Fowlerite, 485
Frit, blue, 494
gum, 494
yellow, 494
flux for, 495
Fuel, 261
choice of, 274
effect of heat on, 267
for lamps, 261
influence of time on, 273
mode of estimating the value of, 273
proper size of, 275
table of relative value of different kinds of, 271
Furnaces, 248
blast, 252
Barron's, 253
cupelling, 250
for baking teeth, 252
measurement of heat of, 275
reverberating, 250
wind, 248
Fusible metal, 407
Fusion-points, table of, 278

G.

Gastric fistula, how to establish, 120
juice, 119
amount of, 128
artificial, 124
chemical characters of, 120
modes of obtaining, 119
physical characters of, 120
Gelatin, sugar of, 58
uses of, 114
Gelatinous group, 50
Gelatinous group, changes of, in digestion, 130
Globulin, 41
composition of, 42
preparation of, 42
physiological relations of, 42
Glucose, 96
in the intestinal canal, 146
tests for, 97
Gluten, composition of, 47
preparation of, 48
Glutin, composition of, 51
physiological relations of, 52
preparation of, 51
reactions of, 50
Glycine, 58, 140
Glycocoll, 58
Glycocholic acid, 71
Gold, 278
alloys of, 312
cupellation of, 287
for plate work, 314
metallurgy of, 284
amalgamation of, 282
bromides of, 324
chlorides of, 322
coins of, chemical composition of, 316
crystals of, 278
foil, 302
fusion of, with galena, 286
black oxide of manganese, 286
oxidating reagents, 284
sulphur, 286
sulphuret of antimony, 285
geographical distribution of, 280
geological situations of, 279
iodide of, 324
leaf, 302
metallic, 303
mixture, 495
ores of, metallurgy of, 280
amalgamation, 282
cupellation, 282
fusion, 282
stamping, 281
washing, 281
oxides of, 305
preparation of, for coloring porcelain, 305

Gold, parting of, from silver, 288
concentrated, 288
dry, 288
by sulphur, 289
wet, 219
by aqua regia, 298
nitric acid, 289
on the large scale, 292
sulphuric acid, 295
Pettenkofer's views of, 297
phosphates of, 311
pigments for painting porcelain, 311
platinum in, 287
scorification of, 284
sponge, 303
sulphurets of, 311
Goldbeating, 300
Guanine, 64
Gum enamels, 497
Hunter's formulæ for, 499

H.

Hæmatin, 100
Hæmatoidin, 101
Haloids, 87
Heat, influence of, on chemical attraction, 235
physical states of bodies, 236
Hindoos, rice ordeal of, 195
Hippuric acid, 67
relations to benzoic acid, 68
Hunter's formulæ, 498
Hydrocarbons, 96
Hydrochloric acid, a constituent of gastric juice, 121
Hydrofluosilicic acid, 453
Hydrogen a constituent of the body, 19

I.

Inosic acid, 71
Intestinal canal, contents of, 146
gases of, 147
juice, 144
chemical characters of, 145
digestive powers of, 145
Iron, a constituent of the body, 21
green stools after the administration of, 150
Iron, titaniferous, 481
Iserine, 481
Jewellery, composition of, 321

K.

Kaolin, 469
composition of, 469
localities of, 469
preparation of, 489
Kremnitz white, 409

L.

Lactic acid, 81
in blood, 83
gastric juice, 82, 121
intestines, 146
muscles, 83
preparation of, 81
Lamps, 240
Berzelius's blowpipe, 241
dentist's, 240
fuel for, 242
Russian, 245
Lead, 403
acetate of, 410
a constituent of the body, 21
alloys of, 407
borate of, 411
bromide of, 408
carbonate of, 409
chloride of, 408
chromates of, 411
fluoride of, 408
iodide of, 408
metallic, 405
metallurgy of, 403
nitrate of, 410
oxides of, 405
phosphate of, 410
phosphuret of, 407
red, 406
sulphate of, 410
sulphuret of, 406
white, 409
Legumin, composition of, 48
preparation of, 49
Leucic acid, 57
Leucine, 56
Lignite, 265
Lime, oxalate of, a normal constituent of urine, 75
relations to respiration, 75
Lipoids, 96
Lipyl, oxide of, 89
salts of, 89
Lithofellic acid, 85

Liver, function of, 142
Lutes. (See Fire-lutes.)

M.

Magnesium, a constituent of the body, 21
Magnus, green substance of, 429
Manganese, a constituent of the body, 21
oxide of, for coloring porcelain, 479
preparation of, 485
Manganocalcite, 487
Margaric acid, 83
Margarin, 91
Meconium, 151
Melanin, 102
Menakan ore, 481
MERCURY, 438
amalgams of, 444
bromides of, 445
chlorides of, 444
effects of, on the system, 446
iodides of, 445
metallic, 441
metallurgy of, 439
mines of, 438
nitrates of, 446
nitruret of, 443
oxides of, 442
phosphates of, 446
phosphuret of, 443
poisonous dose of, 449
sulphates of, 446
sulphurets of, 443
Metacetonic acid, 77
Milk, composition of, 114
globules of, their structure, 46
sugar of, 99
Models, metallic, suitable alloys for, 377, 389, 408, 414
Mouldering of clays, 471
Mucin, 224
MUCUS, 222
albumen in, 227
analysis of, 228
buccal, 227
morbid nasal, 228
morphological constituents of, 223
nasal, 226
origin of, 229
pulmonary, 226
quantity of, 229
reaction of, 223
salts of, 227
MUCUS, supposed action on starch, 184, 190
Murexide, 69
Music metal, 401

N.

Nitrières artificielles, 461
Nitriles, 74
Nitrogen a cause of the instability of animal compounds, 24
a constituent of the body, 19
NITROGENOUS BASIC BODIES, 53
NON-NITROGENOUS ACIDS, 73

O.

Octahedrite, 481
Œnanthylic acid, 79
Oleic acid, 84
in portal blood, 138
Olein, 91
Organic compounds, causes of instability of, 25
mode of union of elements of, 22
illustrated by platinum salts, 430
Osmium, 418
Oxalate of lime, 75
Oxalic acid, 75
Oxygen, a constituent of the body, 19
introduced into the stomach in the saliva, 193

P.

Pancreatic juice, 142
chemistry of, 142
digestive power of, 143
uses of, 145
Parting. (See Gold.)
Peat, 264
Pepsin, 124
preparation of, 125
Schmidt's notion of, 127
Peptones, 129
Petinine, 53
Pettenkofer's test for bile, 86
fallacies of, 138
Pe-tun-tze, 469
Pewter, 400
Phosphorus, a constituent of the body, 19
Picoline, 53
Picric acid, 67
PIGMENTS, ANIMAL, 100
for porcelain, 478
Pitchblende, 483

Plate. (See Silver.)
Plate-work, suitable alloys for, 314
Platinum, 416
action of finely divided, on gases, 425
alloys of, 428
metallurgic treatment of, 422
bichloride of, 436
binoxide of, 427
black, 425
chloride of, 429
coins of, 424
compound bases containing, 430, *et seq.*
geographical distribution of, 417
iodides of, 436
native, 417
nitrate of, 437
nitruret of, 428
oxide of, 426
phosphuret of, 427
preparation of, 417
spongy, 425
sulphate of, 437
sulphuret of, 427
value of, 424
Porcelain, 473
analysis of, 478
contraction of in baking, 477, 490
density of, 477
glaze of, 476
history of, 473
manufacture of at Sèvres, 475
pigments of, 478, 493
Linderer's formulæ for, 487
structure of, 477
tender, 474
true, 475
varieties of, 474
Portal blood compared with hepatic, 138
Potassa, 458
nitrate of, 460
artificial, 460
preparation of, 459
Propionic acid. (See Metacetonic Acid.)
Protein, behavior of reagents towards, 32
compounds, 29
Lehmann's objections to Mulder's theory of, 31
Mulder's view of, 30
teroxide of, 49
Proximate elements, 28
Ptyalin, 159
Berzelius's process for obtaining, 166
Lehmann's process for obtaining, 167
Simon's process for obtaining, 167
reactions of, 167
Wright's, 168
Ptyalism, 199
iodic, 203
mercurial, 199
analysis of fluid of, 202
occasioned by other reagents, 204
Putrefaction, Helmholtz's experiments on, 26
Lewis's experiments on, 27
Pyrometer, Daniell's, 276
Wedgewood's, 275
Pyrosis, fluid of, 197

Q.

Quartation, 290
Quartz, 473
preparation of, 473, 489
Queen's metal, 401

R.

Radicals, compound, 24
Ranula, fluid of, 195
Reiset, yellow salt of, 430
Resinous acids, 85
Rock crystal, 473
Rutile, 481

S.

Saliva, 158
alkalinity of, variations in the, 162, 181
analysis of, 177
analysis of, Lehmann's method, 175
Simon's method, 175
Wright's method, 173
varieties of, 165
acid, 211
relations of to inflammation, 212
acrid, 217
albuminous, 207
alkaline, 214
bilious, 208
bloody, 210
calcareous, 214

Saliva, changes of in various diseases, 220
deficient, 194
digestive action of, 181
on albuminous food, 189, 192
on starch, 181
as compared with other animal fluids, 185
relation of acidity to, 187
elective elimination through, 179
etymology of, 158
fatty, 204
fetid, 216
gelatinous, 219
milky, 221
modes of obtaining for experiment, 158
morbid changes of, 194
morphological elements of, 159
oxygen absorbed by, 172
parotid, 163
cause of alkaline reaction of, 164
specific gravity of, 163
physiology of, 179
Bernard's views of, 183
Liebig's views of, 193
Wright's views of, 181
puriform, 216
quantity of, 159
reaction of, 162
redundant, 196
saline, 215
specific gravity of, 161
affected by ingesta, 161
submaxillary, 164
sulphocyanogen in, 170
variations of, 171
sweet, 206
urinary, 218
varieties of from different glands, 163
Salivary calculi, 231
analysis of, 231
Salivary diastase, 191
Sal prunelle, 462
Salts, composition of, 87
Sarcina ventriculi, 148, 198
Sarcosine, 57
Sebacic acid, 80
Silicic acid, 451
Silicon, 450
a constituent of the body, 19
bromide of, 453
chloride of, 453
oxide of, 451
preparation of, 450
sulphuret of, 453
Silver, 325
alloys of, 345
metallurgic treatment of, 329
by cupellation, 330
by crystallization, 335
by humid process, 336
in presence of mercury, 340
by liquation, 335
by scorification, 329
arseniate of, 363
borate of, 362
bromide of, 367
carbonate of, 362
carburets of, 345
chlorate of, 362
chloride of, 356
reduction of in the dry way, 337
reduction of in the wet way, 338
chromate of, 363
coins, table of, 347
fluoride of, 358
fulminating, 343
German, 378
hyposulphate of, 339
iodate of, 362
iodide of, 337
metallic, 341
native, 325
nitrate of, 361
nitrite of, 361
ores of, 325
amalgamation of, 326
Mexican method, 326
Saxon method, 327
metallurgy of, 326
smelting of, 328
oxide of, 342
perchlorate of, 362

Silver, periodate of, 362
peroxide of, 344
phosphates of, 361
phosphuret of, 345
plate, 355
siliciuret of, 345
silico-fluoride of, 358
subchloride of, 357
suboxide of, 342
sulphate of, 358
sulphite of, 359
sulphuret of, 344
Soda, 463
carbonate of, 464
Sodium, 463
an element of the body, 20
Solder, gold, 315
silver, 346
brass, 379
Speculum metal, 377
Sphene, 480
Starvation, phenomena of, 118
Stearin, 91
Substitution theory, 24, 25
Succinic acid, 79
Sugar, convertible into fat, 114
destination of, 113
in the liver, 139
Sulphocyanide of potassium, determination of, 170
influence on digestion, 192
physiological use of, 193
quantity of affected by ingesta, 171
Sulphur, a constituent of the body, 19
Surcharge, 291
Syntonin, 41

T.

Tartar, 231
analysis of, 233
Taurine, 66, 140
Taurocholic acid, 72
Teeth, 153
composition of at different ages, 155
composition of in the two sexes, 156
effect of putrid food, &c. on, 156
of an ox, 155
porcelain, history of, 487
preparation of materials for, 488
Tin, 394
alloys of, 400
Tin, borate of, 403
bromide of, 402
chlorides of, 401
geographical distribution of, 394
iodide of, 402
metallic, 396
metallurgy of, 395
nitrate of, 403
oxides of, 397
phosphate of, 403
phosphuret of, 400
purification of, 396
sulphates of, 402
sulphurets of, 399
Titanic acid, 480
preparation of, 482
Titanium, 480
ores of, 480
Tonsils, concretion of, 234
Trommer's test for grape-sugar, 97
Troostite, 485
Turf, 364
Type-metal, 407
Tyrosine, 56

U.

Uranite, 483
Uranium, oxide of, 483
Urea, 59
composition of, 60
formation of, 63
hydrochlorate of, 60
in the blood, 62
nitrate of, 60
oxalate of, 61
physiological relations of, 62
quantitative estimation of, 61
secreted by gastric glands, 132
tests for, 61
Uric acid, 68
in fevers, 70
gout, 71
physiological relations of, 70
products of the decomposition of, 69
relations of to oxidation, 71
tests for, 70
Urine pigment, 103
Urobenzoic acid. (See Hippuric Acid.)
Uroerythrin, 104
Uroglaucin, 104
Uroxanthin, 104
Urrhodin, 104

V.

Valerianic acid, 78
Vomited matters, 148

W.

Water, its use in the body, 118
Wood, as fuel, 262
ashes of, 264
loss of heat in green, 263
specific gravity of, 263
ultimate composition of, 264
water in, 262

X.

Xanthine, 63

Zinc, 387
alloys of, 391
borate of, 394
bromide of, 392
Zinc, carbonate of, 394
chloride of, 391
dithionate of, 393
fluoride of, 392
iodide of, 392
metallic, 388
nitrate of, 393
oxide of, 390, 485
perchlorate of, 393
phosphate of, 393
phosphuret of, 391
purification of, 388
sulphuret of, 390
sulphate of, 392
sulphite of, 393

THE END.

LINDSAY AND BLAKISTON

MOST RESPECTFULLY CALL THE ATTENTION

OF THE

MEDICAL PROFESSION,

THROUGHOUT THE COUNTRY,

TO

THE PHYSICIAN'S POCKET VISITING LIST,
DIARY AND MEMORANDUM BOOK,

PUBLISHED ANNUALLY BY THEM.

THE PHYSICIAN'S POCKET VISITING LIST,
DIARY AND MEMORANDA FOR 1854,

WILL BE PUBLISHED EARLY IN AUGUST,

Containing a Visiting List for every day in the year; Memoranda pages for each month; pages for Obstetric Engagements, for Vaccination Engagements, and for accounts asked for and delivered.

It is an invaluable pocket companion for every physician: compact, easily carried in the pocket, methodical in its arrangement, and so useful that the physician, once using it, will never afterwards be without it.

Price, prepared for	twenty-five	patients weekly,	plain, . . .	50 cents.
Do.	do.	do.	tucks, . . .	75 "
Do.	fifty	do.	plain, . . .	75 "
Do.	do.	do.	tucks, . . .	$1 00

"Messrs. Lindsay and Blakiston have laid the Profession under great obligations for one of the greatest conveniences ever furnished them. Here is a little pocket-book, half an inch thick, six by three in dimensions, which will hold all memoranda of visits paid and to be paid for each day of each month during the year; of obstetrical engagements; things wanted and lent; the addresses of patients and nurses; bills and accounts asked for, &c. &c. With it in one's pocket, everybody's bill can be made out in a few minutes. It is the most complete thing we ever saw, and every practitioner would secure one if he could see it."—*Stethoscopist.*

The above work was commenced in 1852, and has met with such universal favor from the Profession, that it is considered superfluous to say more to those who have not yet had one. GIVE IT A TRIAL.

LINDSAY & BLAKISTON,

Publishers and Booksellers,

No. 25 South Sixth Street, above Chestnut.

MEDICAL.

VELPEAU'S ILLUSTRATED MIDWIFERY. Fifth American from the last French edition, with numerous additions and illustrations, by Prof. C. D. Meigs and W. Byrd Page, M.D. 8vo., sheep, ... $3 50

CAZEAUX'S MIDWIFERY, including the Diseases of Pregnancy and Parturition. 116 illustrations. 8vo., sheep, ... 3 00

☞ This work has received the almost universal commendation of the Medical Press and Profession of this country.

CRAIGE'S GENERAL AND PATHOLOGICAL ANATOMY. Royal 8vo., . 3 00

MEIGS' PRACTICAL TREATISE ON THE DISEASES OF CHILDREN. Second edition, much enlarged. 8vo., sheep, ... 3 00

MENDENHALL'S MEDICAL STUDENTS' VADE-MECUM. Being a Compendium of Anatomy, Surgery, the Practice of Medicine, &c., &c. The Third edition, enlarged, with numerous illustrations. Royal 12mo , . 2 50

WALTON'S OPERATIVE OPHTHALMIC SURGERY. 167 illustrations. 8vo., 3 00

HEADLAND'S TREATISE ON THE ACTION OF MEDICINES IN THE SYSTEM. 8vo., ... 1 50

THE PHYSICIAN'S VISITING LIST, DAY-BOOK, AND MEMORANDA, published each year, for twenty-five patients. Cloth, 50 cents; tucks, 75; pencils, 75. Ditto, for fifty patients. Cloth, 75 cents; tucks, . 1 00

A GERMAN-ENGLISH AND ENGLISH-GERMAN CLINICAL PHRASE-BOOK; or, Conversation between Physician and Patient, intended for Hospital, Dispensary, and Private Practice. By Montgomery Johns, M.D. 18mo , ... 1 25

HENLE'S TREATISE ON GENERAL PATHOLOGY. Translated by H. C. Preston, M.D. 1 vol., 8vo., ... 2 00

STILLE'S ELEMENTS OF GENERAL PATHOLOGY. 1 vol., . . 1 50

TUCKER'S PRINCIPLES AND PRACTICE OF MIDWIFERY, . . 1 50

BARTH AND ROGERS'S MANUAL OF AUSCULTATION AND PERCUSSION, ... 63

REESE'S ANALYSIS OF PHYSIOLOGY. A new and enlarged edition, . 1 50

MURPHY'S REVIEW OF CHEMISTRY FOR STUDENTS, . . . 1 00

BIDDLE'S REVIEW OF MATERIA MEDICA AND THERAPEUTICS, FOR STUDENTS With illustrations. Cloth, ... 1 00

HASTINGS' MINOR SURGERY; the Application of Dressings, &c., &c. With 143 illustrations. Cloth, $1 38. Sheep, ... 1 50

MACKINTOSH'S PRACTICE OF MEDICINE. By Morton. Third edition, 3 00

LECTURES ON YELLOW FEVER. Cloth, ... 50

COXE'S EPITOME OF HIPPOCRATES AND GALEN. 8vo., sheep, . 2 00

MORRIS'S LECTURES ON SCARLET FEVER. 1 vol., 8vo., cloth, . 75

SIMPSON ON THE USES OF CHLOROFORM AND ETHER IN SURGERY, MIDWIFERY, &c. 1 vol., 8vo., cloth, ... 1 25

COMFORT'S THOMSONIAN PRACTICE OF MEDICINE. 4th ed. 8vo., 3 00

PHARMACEUTICAL.

REESE'S AMERICAN MEDICAL FORMULARY, including the Medical Properties and Uses of Medicine. Cloth, $1 38. Sheep, . . 1 50

BEASLEY'S DRUGGIST'S GENERAL RECEIPT-BOOK AND VETERINARY FORMULARY. Cloth, $1 38. Sheep, ... 1 50

BEASLEY'S FORMULARY: A Companion to the Druggist's Receipt-Book and Synopsis of the British and Foreign Pharmacopœias. Cloth, . 1 38

Ditto, sheep, ... 1 50

THE PHYSICIAN'S POCKET PRESCRIPTION-BOOK, containing Lists of Terms, Phrases, Abbreviations, &c., &c. Cloth, 63 cents. Ditto, tucks, 80

WYTHE'S POCKET DOSE AND SYMPTOM BOOK. Cloth, 63 cts. Do, tucks, 80

THE AMERICAN JOURNAL OF PHARMACY. Published by authority of the Philadelphia College of Pharmacy. 6 numbers. Per annum, . 3 00

PERIODICALS.

RANKING'S HALF-YEARLY ABSTRACT OF THE MEDICAL SCIENCES. 8 volumes, sheep, per vol., $2 00. 16 numbers, paper, per no., . 75

Published half-yearly, in February and August, per annum, . . 2 00

To mail subscribers, postage prepaid, when paid for in advance.

THE BRITISH AND FOREIGN MEDICAL REVIEW. London edition. Quarterly. Per annum, ... 5 00

THE MEDICAL EXAMINER, AND RECORD OF MEDICAL SCIENCE. Edited by Francis Gurney Smith, M.D., and J. B. Biddle, M.D. Published monthly. Per annum, ... $3 00

FOR FAMILIES, &c.

SMITH'S DOMESTIC MEDICINE, SURGERY, AND MATERIA MEDICA. With Rules for Diet, Bathing, the Management of the Sick-Room, &c., 1 25

THE FAMILY AND SHIP MEDICINE CHEST COMPANION. With Rules for the Compounding and Administering Medicines, &c., &c. Royal 12mo., 1 50

TILT'S ELEMENTS OF HEALTH AND PRINCIPLES OF FEMALE HYGIENE. 1 vol., royal 12mo., ... 1 25

BULL ON THE MATERNAL MANAGEMENT OF CHILDREN IN HEALTH AND DISEASE. A new and improved edition. 12mo., cloth, . . 1 00

MAYO'S PHILOSOPHY OF LIVING. From the 3d Lond. ed. 12mo., cloth, 75

This is the most thorough treatise on the various temperaments, food, drink, exercise, sleep, bathing, dress, &c.; and along with sound directions for preserving physical health of the mind, which deserves especial attention.

DENTAL.

HARRIS'S DICTIONARY OF DENTAL SURGERY AND MEDICAL TERMINOLOGY. A royal 8vo. volume, sheep, ... 5 00

HARRIS'S PRINCIPLES AND PRACTICE OF DENTAL SURGERY. Fifth edition, greatly enlarged and improved, with over 200 illustrations. 8vo., 4 00

JOURDAIN'S DISEASES AND SURGICAL OPERATIONS OF THE MOUTH. With illustrations. 8vo., sheep, ... 2 50

BOND'S PRACTICAL TREATISE ON DENTAL MEDICINE, as connected with the study of Dental Surgery. 2d edition, enlarged 8vo., sheep, . 2 50

PIGGOTT'S DENTAL CHEMISTRY AND METALLURGY, . . 2 50

FLAGG ON ETHER AND CHLOROFORM IN SURGERY, DENTISTRY, MIDWIFERY, THERAPEUTICS, &c., &c. 12mo., cloth, . . 75

ARTHUR'S MANUAL OF DISEASES OF THE TEETH. With illustrations, 50

HORNER'S STUDENTS' GUIDE IN EXTRACTING TEETH. 12mo., cloth, 50

TOME'S DENTAL PHYSIOLOGY AND SURGERY. With illustrations. 8vo., cloth, ... 3 50

THE AMERICAN JOURNAL OF DENTAL SCIENCE. Edited by C. A. Harris, M.D., and A. A. Blandy, M.D. Published quarterly. Per annum, 5 00

SCIENTIFIC.

MORFIT'S CHEMICAL AND PHARMACEUTICAL MANIPULATIONS. With 423 illustrations. 8vo., cloth, $1 75. Ditto, sheep, . . 2 00

NOAD'S CHEMICAL ANALYSIS, QUANTITATIVE AND QUALITATIVE. With additions by Campbell Morfit, and numerous illustrations. 8vo., cloth, $1 50. Ditto, sheep, ... 1 75

WYTHE'S MICROSCOPIST'S MANUAL; for Students and Others. With numerous illustrations. Second edition, enlarged, . . . 1 25

WYTHE'S CURIOSITIES OF THE MICROSCOPE. Beautifully illustrated with colored and other plates, ... 1 00

DE BOISMONT'S RATIONAL HISTORY OF HALLUCINATIONS, APPARITIONS, VISIONS, &c. From the last French edition. 8vo., . 2 50

MAYO'S POPULAR SUPERSTITIONS, AND THE TRUTHS CONTAINED THEREIN. With an Account of Mesmerism. 12mo., cloth, , . 75

GOD IN DISEASE; or the Manifestation of Design in Morbid Phenomena. By J. F. Duncan. 12mo., cloth, ... 75

WALKER ON INTERMARRIAGE; its Influence on Beauty, Health, and Intellect. A new edition, with eight illustrations. 12mo., cloth, . 75

WRIGHT'S AMERICAN RECEIPT-BOOK; containing 3000 Receipts in all the Useful and Domestic Arts. 12mo., cloth, ... 1 00

OVERMAN'S PRACTICAL MINERALOGY, ASSAYING, AND MINING. 12mo., cloth, ... 75

MANURES; their Composition, Preparation, and Action upon Soils. 18mo., cloth, ... 25

DARLINGTON'S FLORA CESTRICA, or, Botanizing Companion. Royal 12mo., ... 2 00

COULTAS'S PRINCIPLES OF BOTANY, AS EXEMPLIFIED IN THE CRYPTOGAMIA. With illustrations, ... 50

LINDSAY AND BLAKISTON,

PUBLISHERS AND BOOKSELLERS,

No. 25 South Sixth Street, above Chestnut,

Give Special Attention to the MEDICAL BRANCH of their Business,

KEEPING ALWAYS ON HAND,

IN ADDITION TO THEIR OWN PUBLICATIONS,

A LARGE AND FULL ASSORTMENT OF

MEDICAL, SURGICAL, DENTAL, AND SCIENTIFIC BOOKS,

INCLUDING ALL PUBLISHED IN THE UNITED STATES,

Which they Sell at the very Lowest Prices.

ALSO,

HAVING AN AGENCY IN LONDON,

THEY RECEIVE MONTHLY PACKAGES

CONTAINING ALL

NEW BOOKS AND PERIODICALS,

AND IMPORT TO ORDER AT THE LOWEST RATES

ENGLISH, FRENCH, AND GERMAN WORKS.

THEY ALSO RECEIVE SUBSCRIPTIONS FOR

ALL AMERICAN OR FOREIGN

MEDICAL PERIODICALS.

Particular attention will be given to the faithful execution of all orders intrusted to them, which they will guarantee shall be furnished at the very lowest prices.

All of the Publications of H. Bailliere, of London and New York, on hand, or furnished at his prices.

LINDSAY & BLAKISTON,

PUBLISHERS, BOOKSELLERS, AND BOOKBINDERS,

No. 25 South Sixth Street, above Chestnut.

H.R. Abbott
Mem. Lib.

Author Piggot, A. Snowden

Title Chemistry and Metallurgy

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
Under Pat. "Ref. Index File"
Made by LIBRARY BUREAU